doi:10.1017/S1431927622009011
Microsc. Microanal. 28 (Suppl 1), 2022

In Situ Pyrolysis of 3D Printed Microstructures – an ESEM Study

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3D printing emerges as one of the key technologies for applications in mechanics, optics and medical technologies, as this approach allows to easily produce complex structures of printable materials at will [1-3]. Besides the general interest for 3D printed structures, the combination of this technique with the old concept of pyrolysis paves the way for an easy and reproducible miniaturization of the printed structures and the conversion of polymeric into ceramic structures. This opens the door to overcome intrinsic limits in spatial resolution and mechanical stability [4].

Pyrolysis is a century-old concept that was in principle already employed in the treatment of coal to obtain coke and is nowadays gaining more interest in solid waste treatment and recycling. In general, it describes the thermal treatment of materials in an inert atmosphere. However, the details of the pyrolysis process, such as concurring diffusive chemical reactions, gaseous evaporation, the roles of environment or surface area are still only scarcely described.

To close this gap in knowledge we present the case study of an *in situ* pyrolysis process, conducted under different atmospheric conditions in an environmental scanning electron microscope (ESEM). We use 2-photon direct laser writing of a commercial photoresist (IP-Dip) to print microstruts on flexible springs, directly on MEMS chips (DENS lightning heating chips, see Figure 1) [5]. Employing a Nanoscribe system, we printed rectangular microstruts with different lengths and volumes to study the effect of surface area to total volume upon pyrolysis.

In the experimental approach, the microstruts are subjected to temperatures between 400°-500° C and the structural changes are continuously tracked by secondary electron imaging. Besides the investigation of the shrinkage in different structural setups, we dip into the role of the inert surrounding, making use of two different vacuum states accessible in our ESEM: standard high vacuum operation *vs.* partial nitrogen atmosphere at a pressure of 3 mbar.

We track the changes of the microstruts that shrink to more than 50% of the initial sizes and describe the temperature dependency of the structural deformation in high vacuum *via* effective activation energies that are independent of the size and the surface-to-volume ratio of the investigated structures.

Upon changing the environmental conditions, the shrinkage behavior turns out to be fundamentally different, largely kinetically hindered and a prevalence of the surface-to-volume ratio on the final structure size becomes apparent.

When evaluating the data pool by generating master curves we are able to fully describe the dynamic process and extract the characteristic time constants.

To complete the picture of the structural changes involved in the pyrolytically induced transformation, we investigat focused ion beam (FIB) cross sections of the microstruts after thermal treatment (see Figure 2). The cross-sectional samples not only allow insights into the deformation and thus the reshaping of the formerly rectangular structures but also offer the possibility to study local structural changes that can be tracked by electron energy loss spectroscopy in 4D-spectrum images (STEM-EELS-SI). Here, we find the generation of a core-shell structure with a subtly different spectroscopic fingerprint around the deformed microstruts.

Based on our findings, the theoretical description of the pyrolysis process can be improved. We envision that precise tuning of the final mechanical and electronic properties may lead to functional metamaterials beyond structural strengthening applications.

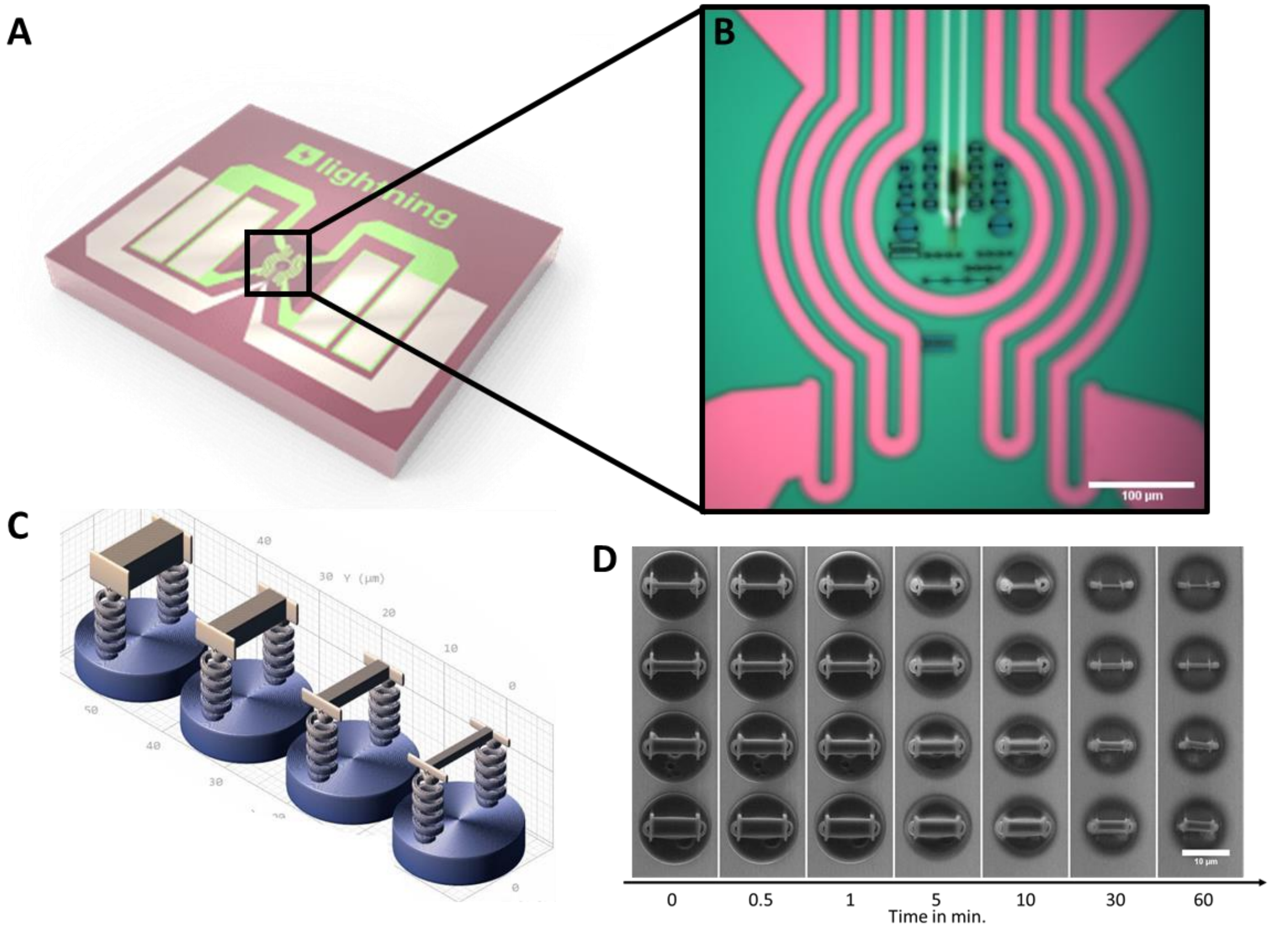

Figure 1. Equipment and studied structures: **A** DENS solutions MEMS chip with heating zone indicated. **B** Light microscopy image of printed microstrut structures contained inside the heating zone. **C** Rendered visualization of studied microstruts with different volumes. **D** Time series montage of in situ heating experiment in SEM.

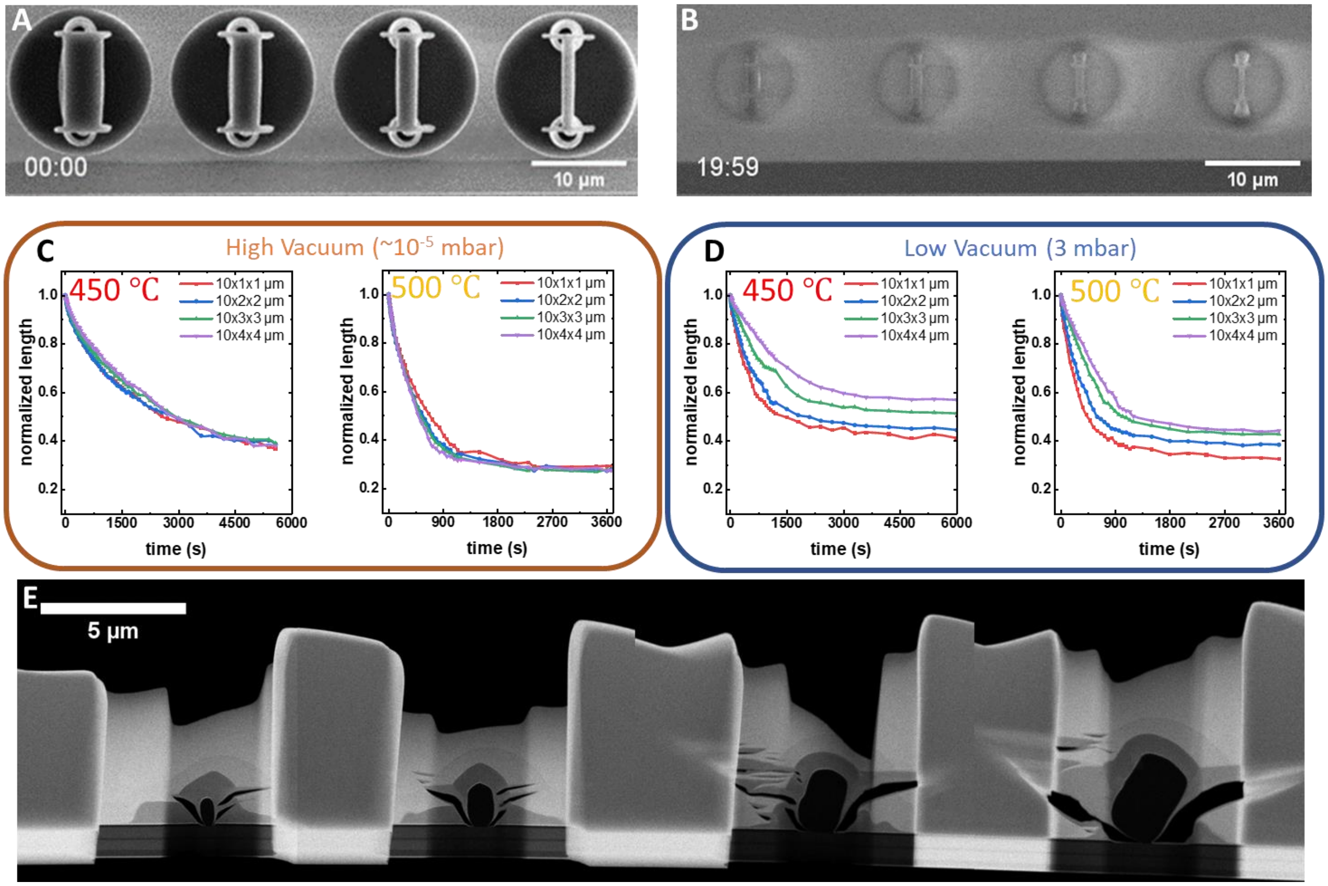

Figure 2. Experimental observation of structural changes: **A** Initial state of unheated microstruts and **B** same area after 20 min @ 500°C. **C** & **D** Evolution of length extracted at 450° and 500° C under high (**C**) and low vacuum (**D**) conditions. **E** HAADF STEM data of cross-sectional FIB lamella of heated and thus shrunken microstruts.

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[6] The authors acknowledge financial funding by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) under Germany's Excellence Strategy *via* the Excellence Cluster 3D Matter Made to Order (EXC-2082/1─390761711)