1 Institute for Applied Materials & Karlsruhe Nano Micro Facility (KNMF), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
2 Thermo Fisher Scientific, Unit 24, The Birches Industrial Estate, East Grinstead, RH 19 1UB, UK
3 Preparative Macromolecular Chemistry, Institute for Chemical Technology and Polymer Chemistry, Engesserstrasse 18, 76131 Karlsruhe, Germany
4 Institute of Zoology and Center for Functional Nanostructures, Haid-und-Neu-Str.9, (MRI), 76131 Karlsruhe, Germany
Corresponding author: michael.bruns@kit.edu

XPS, ToF-SIMS, and HIM Characterization of Functionalized 3D Mesostructures Fabricated by Direct Laser Writing

M. Bruns[1], R. Schwaiger[1], T. S. Nunney[2], A. S. Quick[3], T. Claus[3], B. Richter[4], C. Barner-Kowollik[3]

In recent years significant effort has been spent to develop strategies for the fabrication of structured (bio)polymer modified surfaces on various substrates to alter the properties or to introduce entities with specific functions. These still ongoing activities are mainly stimulated by the wide range of applications in various scientific fields, such as lab-on-a-chip technology, bio-interfaces, and tissue engineering. The utilization of photo-triggered Diels-Alder reactions in combination with shadow masking is an established efficient tool to achieve precise chemically structured surfaces in 2D.[1, 2] However, when aiming at the fabrication of complex 3D structures equipped with different surface functionalities, direct laser writing (DLW) is the method of choice. Most recently developed photoresists comprising e.g. orthogonal thiol-yne chemistry and click chemistry for a subsequent dual surface modification open up a facile avenue to fabricate various structures with several tailored functionalities.[3]

Complementary ToF-SIMS and parallel XPS chemical imaging of chessboard structures

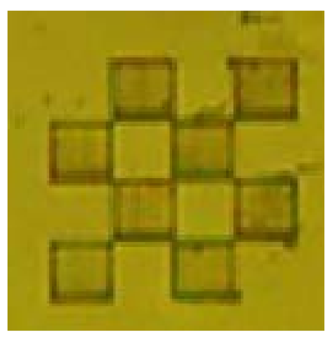
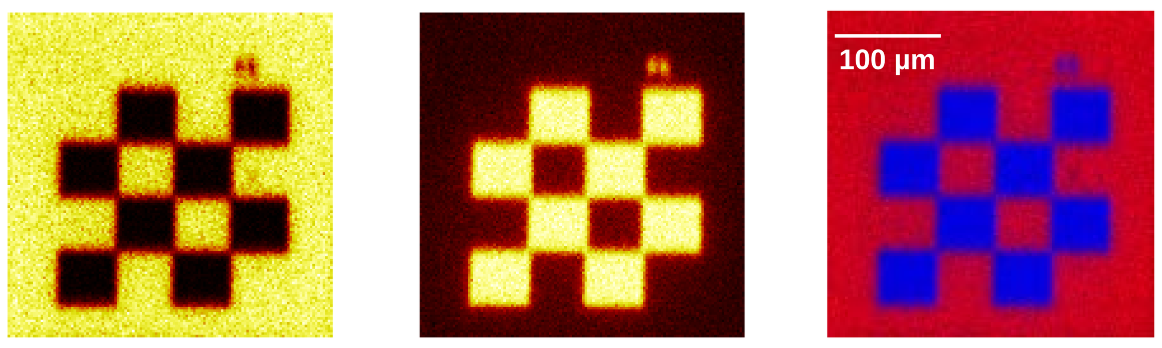
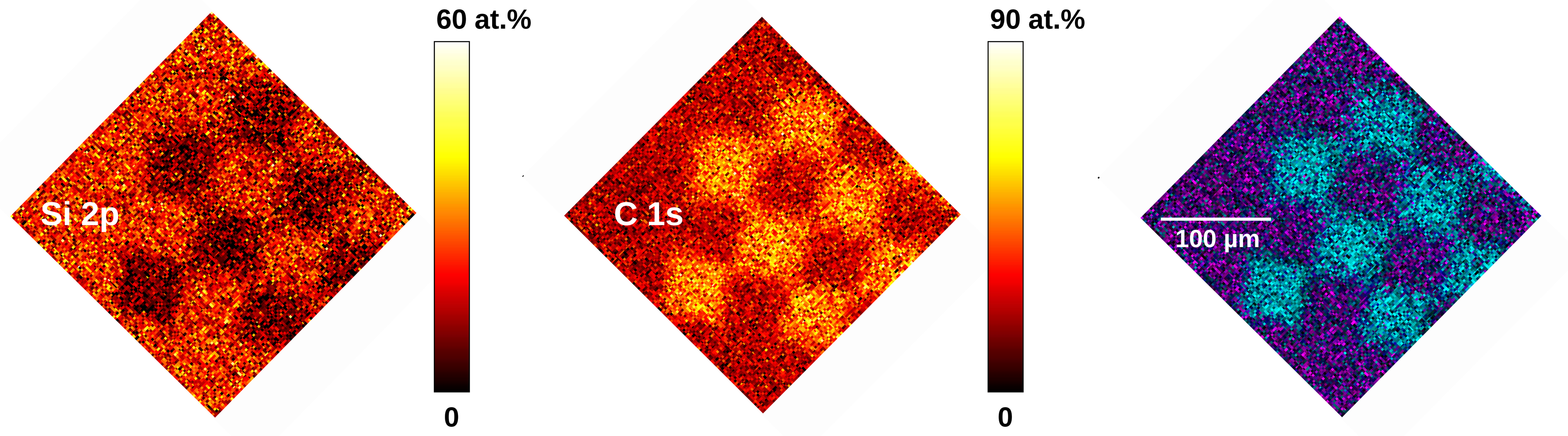


Photo of DLW fabricated chess board structures.



ToF-SIMS (time-of-flight secondary ion mass spectrometry) images of relevant fragments for the glass substrate (**SiO_2^-**, left), the DLW polymer chessboard structure (**$^{79}Br^-$/ $^{81}Br^-$**, middle) and of the corresponding overlay (right).

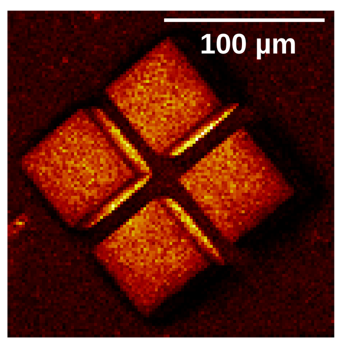


Parallel **XPS** (X-ray photoelectron spectroscopy) images using the **Si 2p** peak for the glass substrate (left) and the **C 1s** peak for the DLW polymer structure (middle) providing quantitative chemical information. The corresponding overlay image is on the right.

Fabrication Strategy

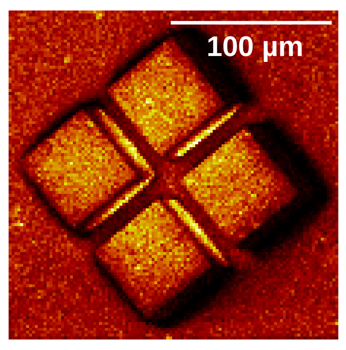
- Using a novel photoresist system for 3D DLW lithography consisting of a **tetrafunctional thiol**, a **tetrafunctional alkyne**, and a **photoinitiator**.
- Exploiting these functional groups as components in corresponding click reactions for the dual post-modification
  - ➔ thiol-Michael addition
  - ➔ copper-catalyzed azide alkyne cycloaddition (CuAAC)

Verification of post-modification of cuboid structures

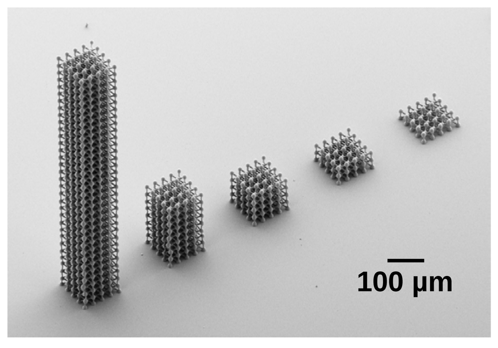


ToF-SIMS images

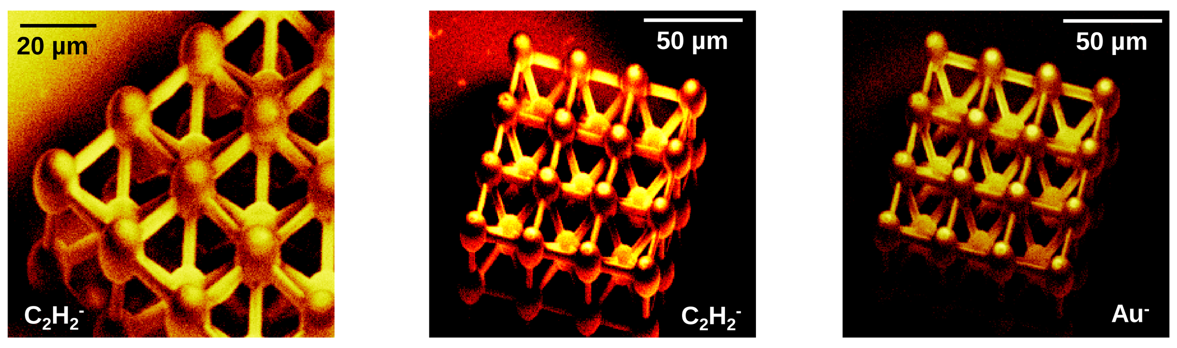
- after thiol-Michael addition ➔ **$^{79}Br^-$** and **$^{81}Br^-$** (left)
- subsequent CuAAC ➔ PEG relevant fragments **C_2HO^-, $C_2H_3O_2^-$, $C_2H_2O_2^-$, $C_2H_3O_2^-$, $C_2H_5O_2^-$** (right). Additional weak unspecific PEG adsorption to the glass substrate.



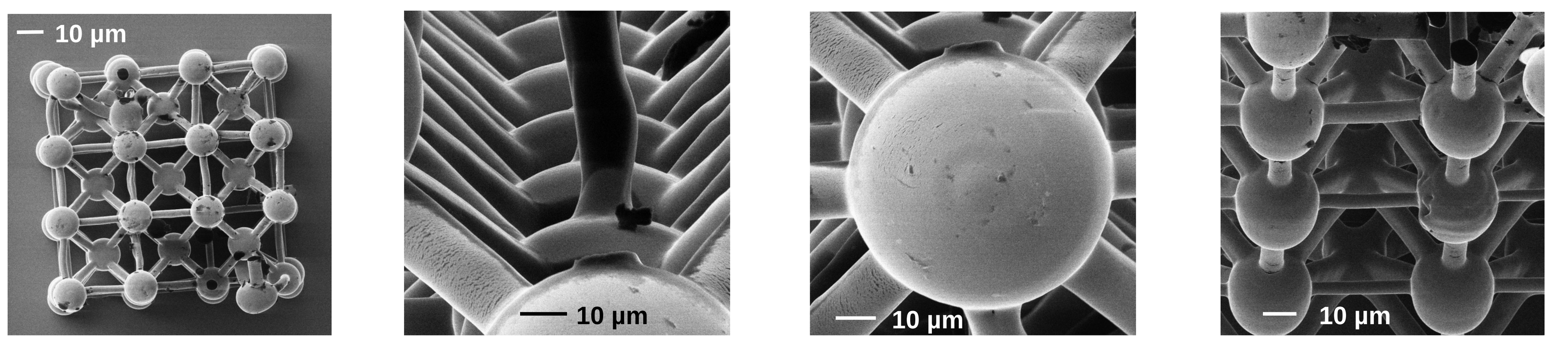
ToF-SIMS and HIM characterization of 3D structures



FE-SEM image of DLW fabricated structures (gold coated).



ToF-SIMS images of a gold coated structure consisting of four layers of 3×3 body-centered cubic unit cells including horizontal bars. **$C_2H_2^-$** represents the adventitious carbon, **Au^-** origins from the gold coating.



Corresponding **HIM** (helium ion microscopy) images of such a gold coated object to prove the structure's geometrical integrity at high spatial resolution and a 10x higher depth-of-field compared to FE-SEM. The Au coating can clearly be distinguished from the polymer structures.

Experimental

Thermo Fisher Scientific K-Alpha XPS-Instrument

- Micro-focused monochromatic AlKα X-ray source, 400 µm spot size

Thermo Fisher Scientific ESCALAB 250 Xi XPS-Instrument

- Micro-focused monochromatic AlKα X-ray source, 250 µm spot size
- Parallel imaging, spatial resolution $\leq$ 3 µm

ION-TOF GmbH ToF.SIMS[5] Spectrometer

- 25 keV Bi_3^+ primary ions, negative polarity
- Spatial resolution 4 µm (HC bunched) and <1 µm (BA)

Zeiss GmbH Orion Plus Helium Ion Microscope

- Edge resolution $\leq$ 0.35 nm
- Acceleration voltage 10-30 kV
- Beam current 1 fA – 100 pA

Conclusions

- Combined complementary ToF-SIMS and XPS imaging provides quantitative images of DLW structures in a non-destructive manner.
- ToF-SIMS enables non-destructive 3D chemical imaging and therefore provides the possibility to evidence differently chemical modified parts of complex DLW structures.
- HIM substantiates the geometrical integrity of such structures at extremely high depth-of-field.
- All combined methods use effective neutralizations systems and therefore are ideal for chemical surface characterization of insulating materials.

References

[1] T. Tischer, T. K. Claus, M. Bruns, V. Trouillet, K. Linkert, C. Rodriguez-Emmenegger, A. S. Goldmann, S. Perrier, H. G. Börner, and C. Barner-Kowollik, Biomacromolecules **14** (2013) 4340−4350.
[2] T. Paulöhrl, G. Delaittre, V. Winkler, A. Welle, M. Bruns, H.G. Börner, A. M. Greiner, M. Bastmeyer, C. Barner-Kowollik, Angew. Chem. Int. Ed., **51** (2012) 1071–1074.
[3] A. S. Quick, A. de los Santos Pereira, M. Bruns, T. Bückmann, C. Rodriguez-Emmenegger, M. Wegener, and C. Barner-Kowollik, Adv. Funct. Mater. 2015, **25**, 3735–3744.