Electron microscopic investigation of photothermal laser printed ZnO nanoarchitectures

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Background incl. aims

Multi-photon 3D laser printing of polymers can be used to create complex structures on the micro- and nanoscale [1,2]. This technique involves focusing a laser into a liquid ink, initiating a reaction that solidifies the material at the laser focus. While this technology has primarily been employed with polymers, recent developments aim to extend its capabilities to inorganic materials. However, these materials often need post-processing at elevated temperatures, facing challenges for multi-material architectures due to the potential impact on polymer structure [3]. Recent advances in the direct printing of semiconducting ZnO through hydrothermal synthesis offer a promising alternative since no post-processing step is needed [3]. This enables the direct laser printing of functional microelectronic devices, possibly combined with polymers. Using electron microscopy, we demonstrate that single crystalline ZnO can be printed on amorphous substrates, opening the possibility of new applications, e.g., non-linear properties for devices in optics. However, a deeper understanding of the growth of the ZnO crystals and the crystal rotation is necessary for further applications in microelectronic devices.

Methods

The ZnO structures are photothermally printed from a liquid ink (zinc formate and sodium citrate in dimethyl sulfoxide) onto a glass substrate using a focused continuous-wave laser (532 nm wavelength).

An FEI Helios G4 FX combined focused ion beam (FIB) and scanning electron microscopy (SEM) dual-beam system was used to characterize the crystallinity and crystal orientation of the printed ZnO with electron backscatter diffraction (EBSD) with a Bruker eFlash detector. EBSD requires a polished sample surface, for which we used FIB milling since the ZnO structure sizes are in the µm range. First, a Pt protection layer is deposited using the FIB. Then, the sample is tilted so that the sample surface is aligned at an angle of 10° relative to the Ga+-ion incidence. After polishing, the sample is tilted to a 70° effective sample tilt relative to the electron beam incidence for EBSD data acquisition. The Bruker Esprit software was used for the collection of the EBSD patterns, data processing, and indexing using the Hough transformation of EBSD patterns to detect the Kikuchi lines . Subsequent orientation analysis was performed using the MTEX toolbox for MATLAB [4], providing, e.g., inverse pole figure (IPF) maps.

Cross-section samples for scanning transmission electron microscopy (STEM) were prepared using the in-situ lift-out technique in an FEI Strata 400S Ga+-ion FIB/SEM instrument. A Pt protection layer was deposited by FIB to protect the underlying material during FIB milling. High-resolution high-angle annular dark-field (HAADF-) STEM images were acquired on an FEI

Titan³ 80-300 at 300 keV. An FEI Tecnai Osiris operated at 200 keV and equipped with ChemiSTEM technology was used for chemical analyses with energy-dispersive x-ray spectroscopy (EDXS). The EDXS data was processed using Bruker Esprit.

Results

The continuous laser is focused at the interface of ink and substrate, resulting in the deposition of crystalline ZnO. Residual ink is removed by a solvent and the ZnO line is left (Fig. 1g).

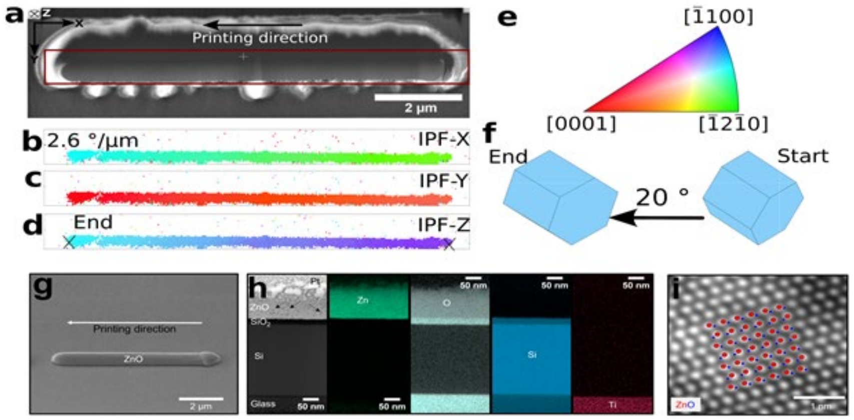
SEM -EBSD was applied to analyze the crystallinity of ZnO (Fig. 1a). Single crystalline ZnO with the wurtzite crystal structure (P63mc) grows on the amorphous substrate for a 1 µm/s printing speed and a laser power of approximately 0.8 mW. The initial ZnO orientation is likely random since different lines show different initial orientations (not shown). In the IPF maps, one large ZnO single-crystal can be identified due to one single general color in each IPF map (Fig. 1b-d). However, a gradient of the color in all IPF maps indicates that the orientation of the crystal varies along the printed line, which means the crystal rotates along the printing direction. The corresponding color legend is presented in a triangle color legend (Fig. 1e). The orientation of the hexagonal lattice of ZnO at the start and the end of the printing is schematically shown (Fig. 1f). Earlier works have reported rotating lattice crystals in Sb-S-I glass system, by using different materials and laser printing parameters [5]. A total misorientation of 20° over the entire printed line (7.9 µm) is observed, corresponding to a linearly changing rotation rate of 2.6°/µm.

STEM-EDXS is used for chemical analysis of a cross-section TEM sample, which shows porous ZnO formed on silica (Fig. 1h). Nanometer-sized pores in the ZnO layer are visible as dark regions in the HAADF-STEM image result from the printing process (marked with arrows) . The Pt layer on the ZnO is deposited by FIB and acts as a protection layer during TEM lamella preparation. Also chemical analysis shows that the substrate layer below ZnO consists of 20 nm SiO2 and the layer below is a 250 nm Si layer. The silica glass under the Si contains Ti. The atomic resolution image shows a small region of the single crystalline laser-printed ZnO, here viewed along the ZnO<2-1-10> zone axis orientation (Fig. 1i). The Zn atomic columns appear bright and the O columns are not visible due to the HAADF-STEM Z-contrast.

Conclusion

To conclude, we provide an extensive electron microscopic examination of ZnO single crystals produced by photothermal laser printing at relatively low printing speed and laser power on an amorphous substrate. EBSD confirms the single crystallinity of ZnO with a rotating lattice over a distance of 7.9 µm. We will explore different printed geometries for a better understanding of the rotating lattice ZnO single crystals and the growth process regarding laser printing parameters. The aim will be to use such laser-printed semiconductor devices in microelectronics applications [3].

Graphic:



Keywords:

Electron microscopy, EBSD, laser-printing, ZnO

Reference:

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