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Solvent-free synthesis of supported ZIF-8 films and patterns through transformation of deposited zinc oxide precursors

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Supplementary information (ESI)

Contents

1. Materials and methods

Sputtering of ZnO

ZnO was deposited by RF magnetron sputtering using a High Vacuum Laboratory System PLS 580 from Pfeiffer. Films with different thicknesses (100, 500 and 1000 nm) were grown on oxidized silicon substrates. The deposition (RF Power: 250W, Bias: 85V) was performed at room temperature at 9.4 10^{-3} mbar (Ar flow: 20 sccm; O_2 flow: 7 sccm). For further processing, the wafers were cut into 10 x 10 mm² pieces.

Microcontact printing of ZnO via sol-gel transformation and calcination

Hexagonal and square 300 mesh copper transmission electron microscopy grids (Agar, USA) were used as stamps for the microcontact printing procedure. Microscopy glasses (Marienfold, Germany) cut in 10 x 10 mm² pieces were used as supports. Following a literature sol-gel deposition,[1] layered basic zinc acetate (LBZA) was first stamped and subsequently converted to ZnO via calcination. The sol-gel precursor solution consisted of 0.5 M zinc acetate dihydrate (99.5%, Merck, Germany) and 0.5 M monoethanolamine (99 %, Janssen Chimica, Belgium) in 2-propanol (100 %, VWR Prolabo, France). The stamps were inked with the sol-gel precursor solution while placed on a paper sheet to absorb the excess solution. After inking, a 1 min evaporation step at room temperature was used before applying the stamps. Stamping was performed by placing the inked stamps on preheated 373 K microscopy glass supports. A second microscopy glass was placed on top of each stamp as a weight. During stamping the sample-support assemblies were placed in an oven at 373 K for 5 minutes. The stamps were then carefully removed. The LBZA patterned supports were then calcined at 10 K min-1 to 723 K and 1 h isothermally at 723 K to obtain a ZnO pattern.

Electrochemical deposition of flake-like ZnO films

The synthesis of flake-like ZnO films was run following the approach of Michaelis *et al.*[2] A three electrode setup was used to electrodeposit the oxide. Pure zinc was used as counter electrode, standard calomel electrode (SCE) was used as reference and polished carbon steel substrates (10 x 30 mm²) were used as working electrodes. The electrolyte consisted of an aqueous solution with the following reagents: 5 mM of $ZnCl_2$ (98 %, Sigma-Aldrich Fluka, Germany) 0.1 M of KCl (99.5 %, Chem-Lab, Belgium) and 0.6 mM of sodium laurylsulfate (99 %, Acros, USA). The solution was heated at 343 K and kept stirred both with a magnetic bar and a continuous flow of oxygen gas. The films were deposited at -1 V vs reference for 10 minutes with a potentiostat (EG&G, model 273). For further processing, the working electrodes were cut into 10 x 5 mm² pieces.

Solvent-free transformation of supported ZnO films to ZIF-8 films

The 2-methylimidazole (HmIM, 99 %, Acros Organics, Belgium) powder was finely ground in a mortar. The samples were each placed at the bottom of glass crimp cap reactors and covered with a thin layer (approximately 30 mg cm^{-2}) of HmIM. The reactors were capped and placed in an aluminum heating block at 433 K. The reaction time was monitored from the point of melting. To interrupt the reaction at different time points, the reactors were removed from the heating block and instantly cooled to ambient conditions in a water bath. After cooling down to ambient conditions the samples were removed from the reactors and rinsed with methanol to remove the remaining HmIM. The samples were then left at ambient conditions to dry.

Characterization

Scanning electron microscopy images were recorded using a Philips XL30 FEG. For cross-sectional imaging, the supporting wafer was simply broken. The samples were sputtered with gold before analysis.

XRD patterns were recorded on a STOE STADI MP in Bragg–Brentano mode (2θ – θ geometry; Cu Kα_1) using a linear position-sensitive detector: step width 0.5° 2θ, scan rate= 1520 s per step (2θ=5–20°; Δ2θ=0.01°). Reference diffraction patterns were simulated from cif-files using CCDC Mercury 2.4.[3] Material cif-files were retrieved from the CCDC database[4] and the AMSCD database.[5]

The tape test was performed by manually pressing commercial insulating tape on top of the film and subsequently peeling it off in a quick movement.

2. **Additional figures** (Fig S1-S6)

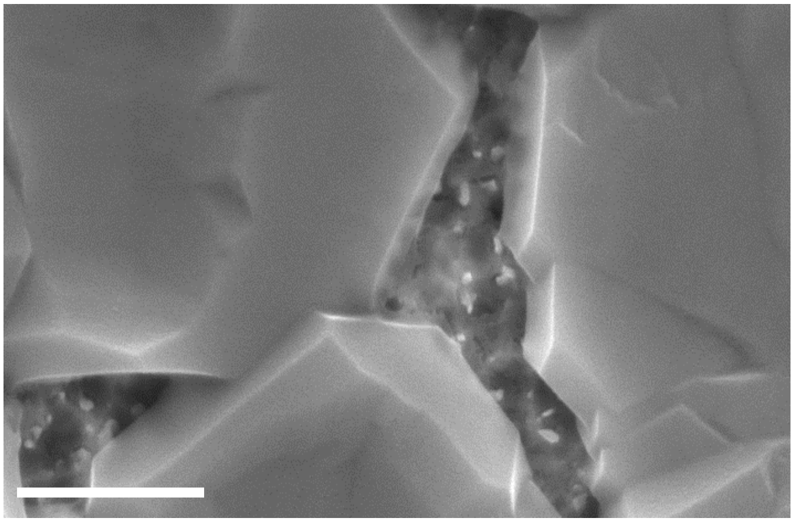

Fig. S1 SEM image showing the 1 µm thick sputtered ZnO sample after 1 min contact time with melted mIM. This detailed image shows the leftover ZnO film between the ZIF-8 crystals. Scale bar: 1µm

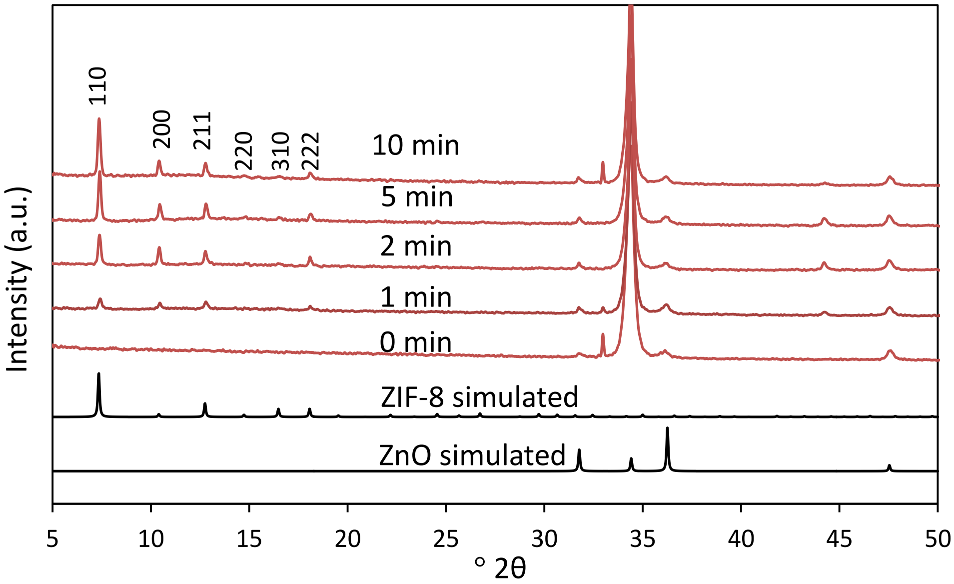

Fig. S2 Reflection XRD patterns of the resulting films at different times during the transformation of 1 µm sputtered ZnO films on silicon wafer supports.

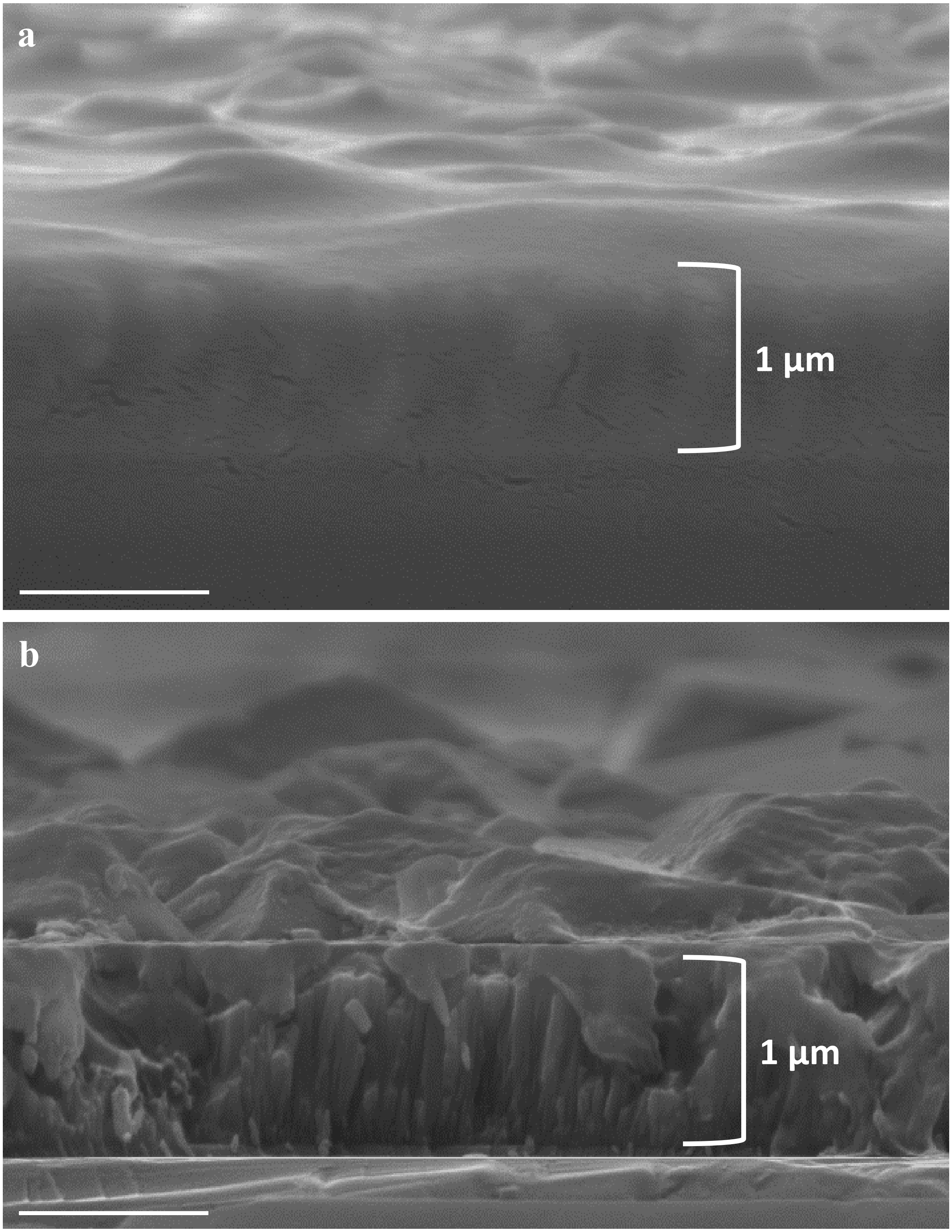

Fig. S3 SEM image of the cross-section of (a) the 1 μm thick ZnO film and (b) the resulting ZIF-8 film after 10 min transformation. Scale bars: 1 μm

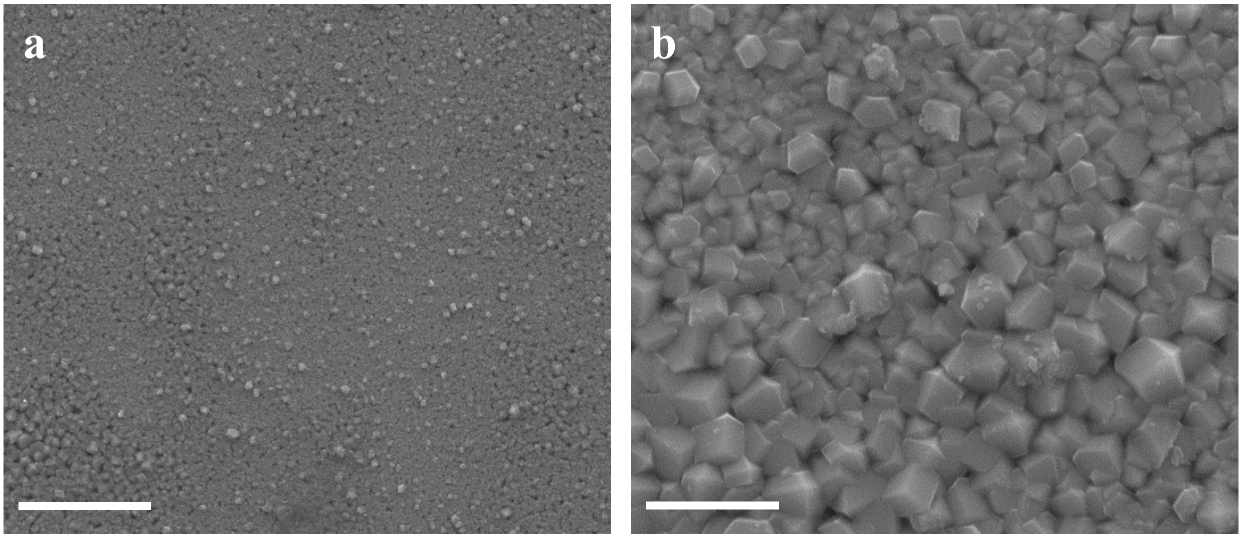

Fig. S4 SEM images of the intact ZIF-8 film (formed by 5 min transformation of a 1 µm thick ZnO film) after pressing adhesive tape (in this case generic insulator tape) on the film and peeling it off. Scale bars: (a) 20 µm and (b) 5 µm

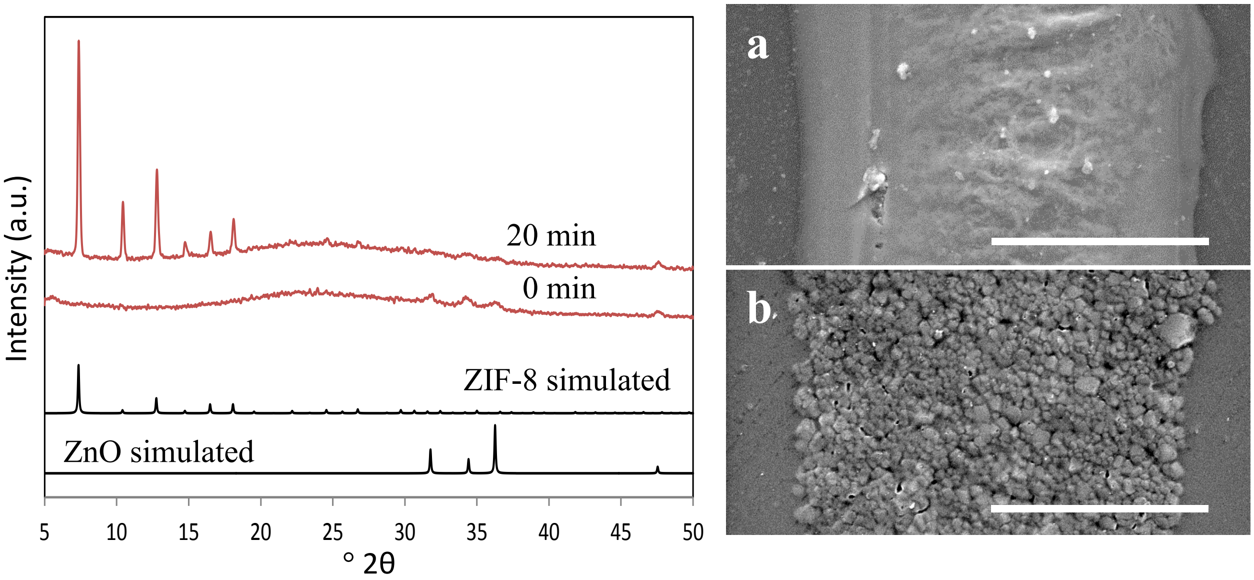

Fig. S5 Right: high magnification SEM images of the ZnO pattern and resulting ZIF-8 pattern after transformation showing the sharp replication of the pattern edges. (a) ZnO pattern before transformation, (b) ZIF-8 pattern after 20 min transformation. Scale bars: 5 µm. Left: reflection XRD patterns measured before and after 20 min transformation and simulated reference patterns.

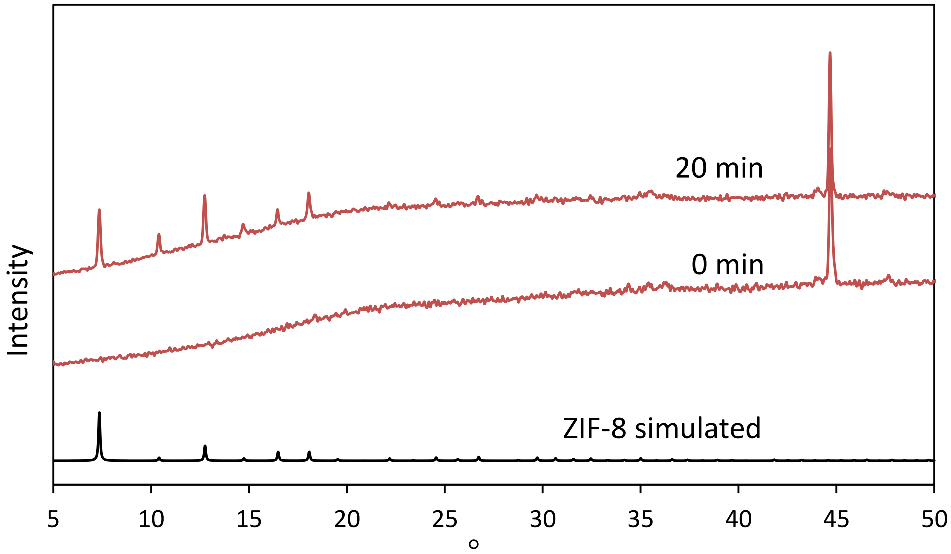

Fig. S6 Reflection XRD patterns of the flake-like ZnO film on carbon steel support and the resulting flake-like ZIF-8 film after 20 min transformation.

3. References

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