Nanowires growth in FIB-SEM reactor

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In-situ SEM imaging of heat & gas mediated processes such as chemical vapor deposition, reduction, or oxidation is enabled by a new reactor dedicated FIB-SEM systems. The design combines sample heating (up to 1200°C) by a micro-heating-plate [1] and possibility for gas injection into a differentially pumped reaction space of low volume (2 microliters) surrounding the heated sample. Compared to in-situ SEM observation of gas & heat mediated processes in the whole SEM chamber [2] [3], the FIB-SEM reactor enables operation in cleaner environment, minimizing sample oxidation or contamination. Defined flow pattern in the sample area, higher (up to 100 Pa), controllable and measurable pressure inside the reactor are clear benefits compared to gas injection from a needle. Already available reactors with sub-microliter reaction volume closed between two MEMS chips (dedicated mainly for in-situ imaging in TEM) allow inspection of liquid samples or sub-micron particles dissolved in a liquid carrier only. Design of the FIB-SEM reactor provides possibility for processing of any bulk sample placed on a SEM holder.

Sample preparation in a FIB-SEM system is done in following steps. Upper side of the reactor formed by a pressure limiting aperture (Figure 1) is removed and part of the bulk sample extracted by FIB milling is placed to the micro-heating-plate using a manipulator needle [4]. Sample can be glued to the heating-plate by FIB/SEM assisted (typically Pt or W) deposition. In the last sample preparation step, the pressure limiting aperture is mounted on top of the reactor to close the reaction volume and assure desired overpressure in the sample area. Low gas flow through the hole in the aperture allows for high vacuum operation of the SEM chamber, which is needed for high resolution imaging. Detection of secondary and backscattered electrons is possible, preferably using in-lens detectors, as both signal electrons can pass through the pressure limiting aperture. Simultaneous STEM imaging through thinned windows in the micro-heating-plate is possible as well.

In-situ observation of nanowires growth in the FIB-SEM reactor was done in the Thermo Scientific Helios G4 UX in high resolution mode using in-lens detector (TLD). Example of rutile nanowires growth from acetone vapor on a titanium substrate heated to 850°C is shown in Figure 2 and in movie [5]. Platinum-gallium nanowires growing at the presence of hydrogen at 700°C are shown in Figure 3 and in movies [6], [7]. Figure 4 shows sequence of tungsten oxide nanowires formation from WS_2 tube heated to 725°C.

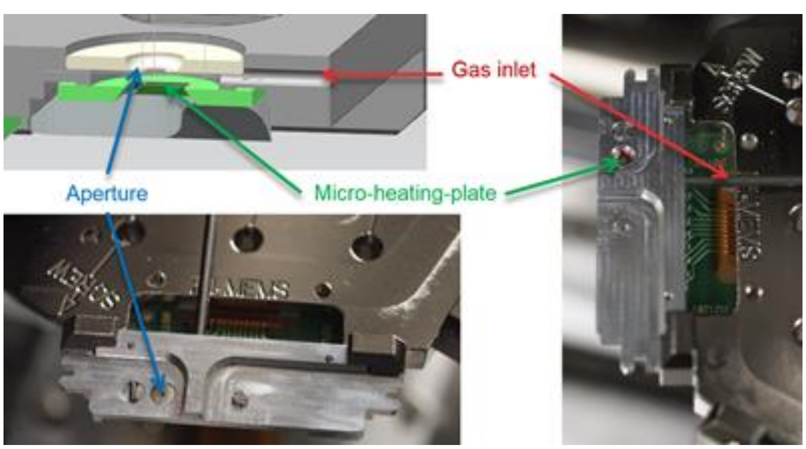

Figure 1. FIB-SEM reactor connected to multi-sample holder of a Helios G4 UX system, which controls heating of the micro-heating-plate (up to 1200°C). Pressure limiting aperture separates overpressure in the reactor (up to 100 Pa) from vacuum environment ($<10^{-2}$ Pa) in SEM chamber.

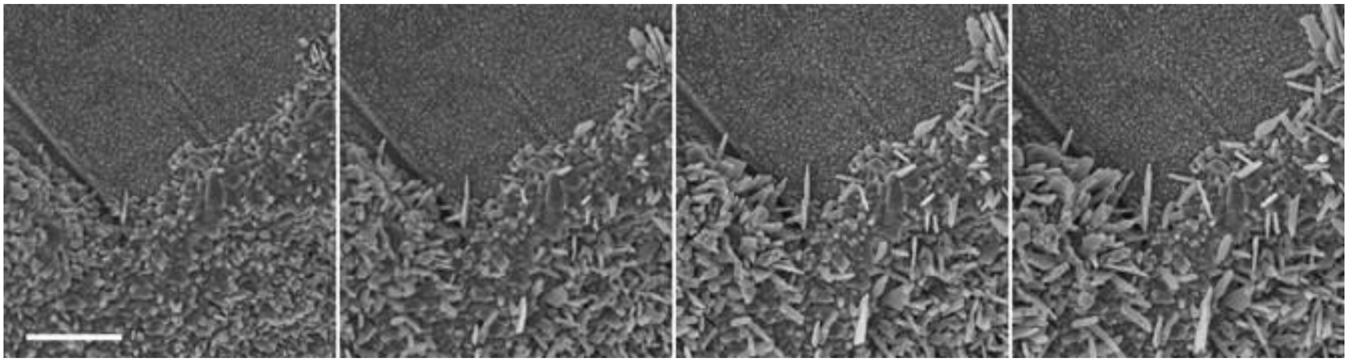

Figure 2. Evolution of rutile (TiO_2) nanowires in acetone vapor (100 Pa) on Ti substrate heated to 850°C in FIB-SEM reactor. Time step between images: 4 minutes. Scale bar: 2 µm.

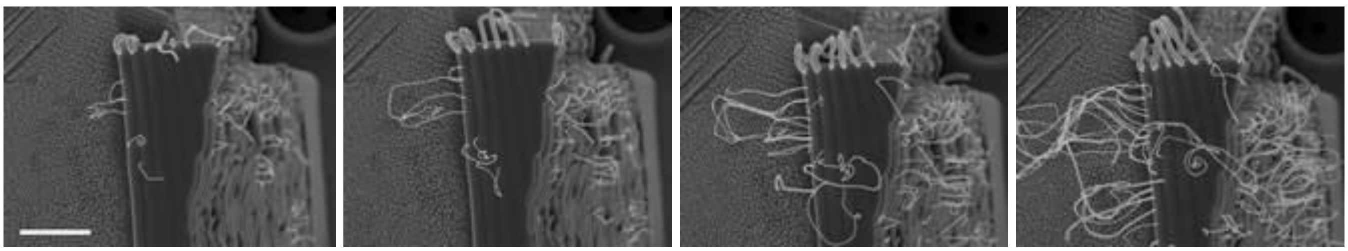

Figure 3. Nanowires growing from Pt-Ga substrate (platinum deposited by Ga FIB) at 700°C in pure hydrogen environment (H_2 pressure: 50 Pa). Average time interval between images: 1.5 minute. Scale bar: 4 µm.

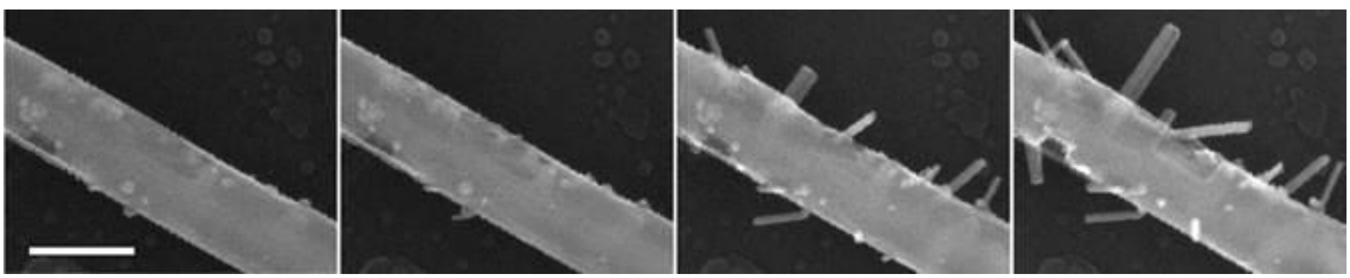

Figure 4. An image sequence (6 minutes duration) of tungsten oxide nanowires growth from tungsten disulfide nanotube during oxidation reaction (725°C, H_2O vapor in reactor). Scale bar: 100 nm.

References:

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[6] https://www.youtube.com/watch?v=RGqaQj07Wfc&feature=em-share_video_user
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