Focused Ion Beam Induced Synthesis of a Porous Antimony Nanowires Network

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Introduction

While the generation of 0-D nanostructures such as quantum dots with defined properties can be managed since a while, there is a remarkable increasing scientific and technological interest in 1-D nanostructures. During the last decade significant progress has been made in the realization of appropriate 1-D nanostructures, either by top down approaches issuing lithography and dry etching techniques, as well as bottom-up growth techniques such as electrochemical deposition within porous templates, e.g. anodic alumina membranes, or catalyst assisted chemical vapor deposition. Very recently nanowires of different types of material have been grown by the vapor-liquid-solid (VLS) mechanism, in which various metals such as Au, Fe, Ti or Ga catalytically enhance the growth of nanowires. Thereby a liquid alloy cluster serves as a preferential site for catalytic adsorption of reactants from the vapor phase and – when supersaturated – as the nucleation site for crystallization. The supersaturation of the eutectic melt acts as the driving force for the growth in a highly anisotropic manner. However, there is still an on-going effort in developing synthesis methods with the main goal to grow nanowires at moderate temperatures in order not to damage preexisting modules and to grow them at a specified location while eliminating the requirement of a later assembly process.

Experimental

Thin lamellas of antimony samples with purity > 99.999% were prepared and cleaned by rinsing with acetone and isopropyl alcohol followed by blow-drying with pure nitrogen. The used focused ion beam (FIB) system was equipped with a liquid Ga metal ion source. For the purpose of patterning the FIB is scanned over a predefined area in discrete steps with well-defined step size and dwell time, i.e. the time the beam remains on each single spot. Each scan across the selected area deposits an ion fluence which is correlated to the above mentioned parameters. Single pass milling denotes a scanning strategy where the desired fluence is deposited within one single scan. For multi pass milling, the beam is scanned several times across the predefined area and the total ion fluence is dependent on the number of scan repetitions of the FIB. The topographical and compositional evolution of the Sb surfaces irradiated by focused Ga beam is investigated by means of scanning electron microscopy (SEM), Auger electron spectroscopy (AES), high resolution transmission electron microscopy (HRTEM), selected area diffraction (SAD), and energy dispersive X-ray diffraction (EDX) measurements.

Results

Figure 1(a) shows a secondary electron microscopy (SEM) image of the Sb surface after multi pass milling of a (2x2) μm^2 wide box with a 100 times higher ion fluence of

$6.2x10^{18}$ Ga ions/cm^2. As expected, FIB exposure leads to effective sputtering of the substrate material with a high sputter yield of approximately 14.3 sputtered Sb atoms per incident Ga ion. The rim of the several micrometer deep hole is surrounded by a dense network of nanofibers which show very uniform diameters in the range of 25 nm. Milling the same box with the same ion fluence in single pass mode leads to the formation of a pattern shown in Fig. 1(b). Thereby the FIB scan starts in the upper left of the box and moves along in serpentines with a pixel and line spacing both of 10nm, which guarantees a nearly uniform ion fluence distribution. The whole FIB modified area is covered by nanofibers with the exception of the last line scan routed from the lower right to the lower left edge. Nanofibers reach even 2 µm beyond the rim of the FIB milled area. Fig. 1(c) shows the Sb surface after single pass milling viewed under a tilt angle of 75°. The FIB generated nanowire extrusions do not form a plane porous disc as one could assume from the top view SEM image in Fig. 1(b). As shown in the schematic of Fig. 1d, the nanofibers appear on a ramp-like base normal to the plane rising along the scan direction of the FIB.

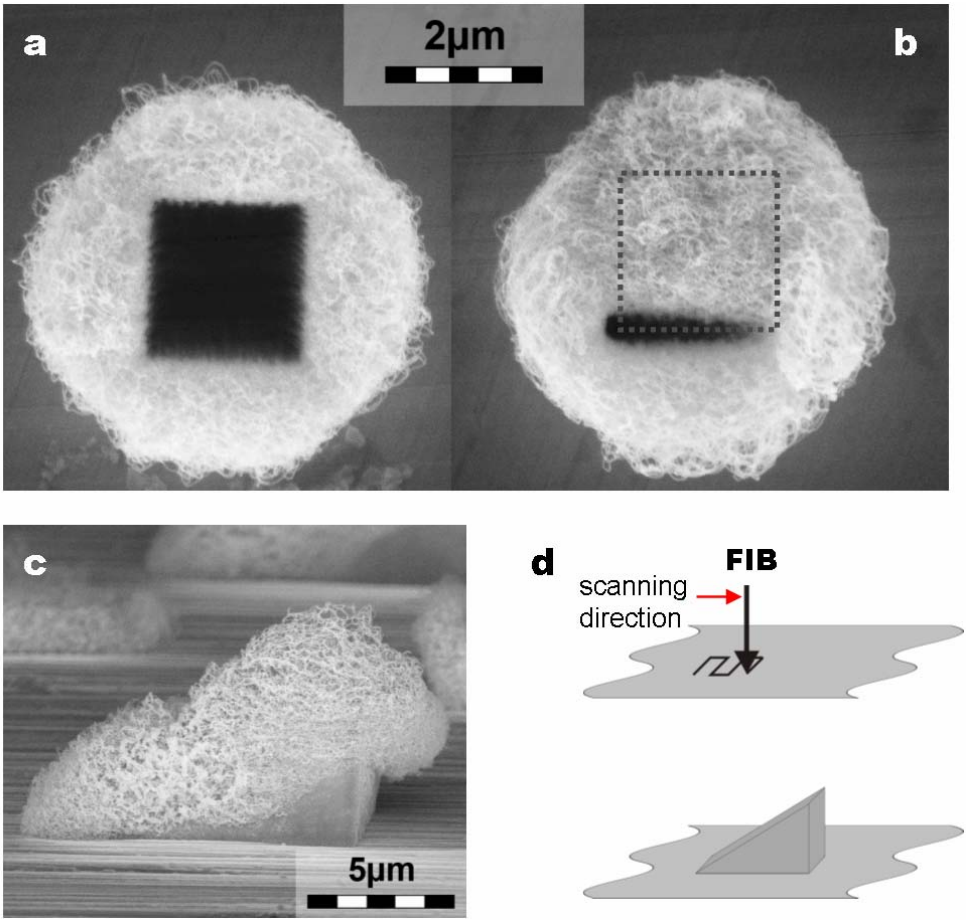

Fig. 1: Sb surface processed using a 50keV Ga FIB with an ion current of 200pA. (2x2) µm^2 milling areas irradiated by an ion fluence of $6.2x10^{18}$ ions/cm² in (a) multi pass mode and (b) single pass mode, tilted view SEM image of a (10x10) µm^2 milling area (c) exposed to an ion fluence of $3.1x10^{18}$ ions/cm² processed in single pass mode, schematic sketch (d) visualizing the FIB scanning strategy and the resulting uplifted nanofiber network.

The formation of this ramp-like structure is a result of the pixel-by-pixel and accordingly of the line-by-line scanning strategy. Scanning the first line of the predefined milling

area leads to nanofiber growth even beyond the ion irradiated region. By the guidance of the FIB through the subsequent lines, nanofibers which were grown on the not yet exposed part in the forefront of the scanning beam are removed by sputtering. Nanofibers in already irradiated zones, i.e. behind the scanning beam, remain unaffected. These nanofibers form a network which is further densified by redeposited Sb. Due to the ongoing FIB scanning this nanofiber network reduces the escape angle for the sputtered Sb and more and more of them are picked up by the network which leads to an upraising of the structures.

The cross sectional SEM image of a (10x10) μm^2 milling box in Fig. 2 shows the porous material covering the surface and the FIB milled box. The range of the porous nanofibers network generated by the impact of the FIB reaches some microns beneath the surface level.

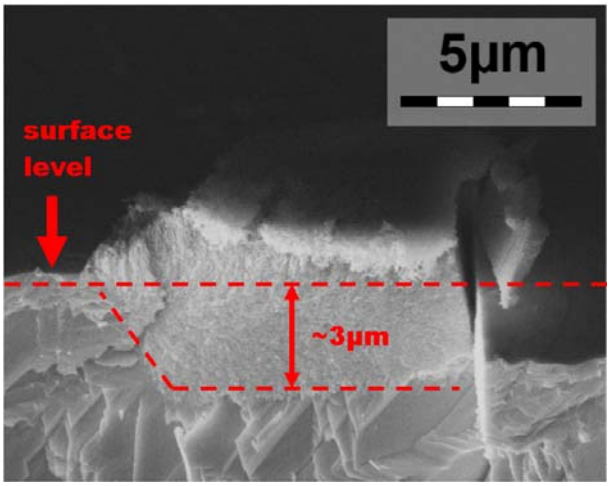

Fig. 2. SEM image of the cross sectional view of a FIB milled (10x10) μm^2 area accomplished by cleaving the sample. The porous network at the FIB exposed area using an ion fluence of $3.1x10^{18}$ ions/cm^2 reaches several micrometers in depth.

Extensive transmission electron microscopy (TEM), selected area diffraction (SAD), Auger electron spectroscopy (AES), and energy dispersive X-ray spectroscopy (EDX) of individual nanofibers prove that they are completely amorphous even in the nanometer scale and consist of pure antimony. The TEM image in Fig. 3(a) shows the exceptionally uniform diameters of the nanofibers of about 25 nm along their entire length.

The FIB modified samples covered by the nanofibers were annealed in a special furnace setup which allows processing at well-controlled temperature profiles in He atmosphere. Several experiments showed that the temperature ramp is a crucial parameter for the grain size of the resulting re-crystallized structure whereby the diameter and shape of the nanowires remain unaffected by the annealing. The high resolution TEM (HRTEM) image in Fig. 3(b) displays a Sb nanowire after moderate thermal annealing at 453 K for 30 min. The diffraction pattern in Fig. 3(c) shows the most prominent (110) and (120) reflections for Sb with its trigonal crystal structure, and the lattice parameter of 0,354 nm is consistent with the tabulated value for bulk Sb.

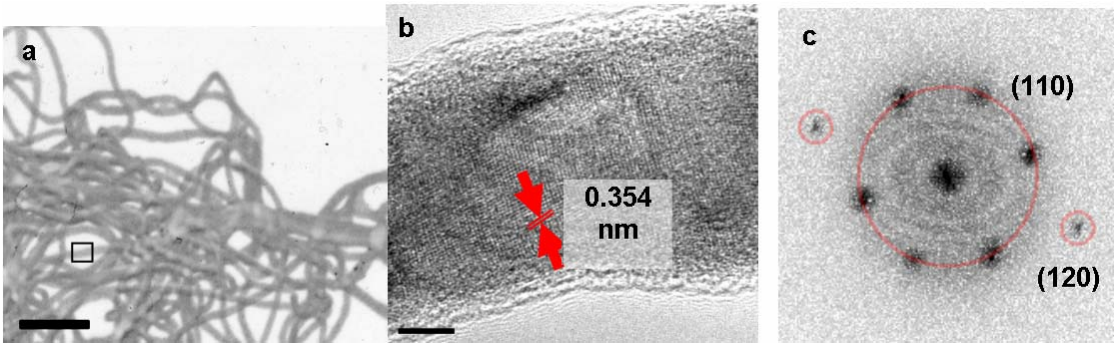

Fig. 3. The low magnified TEM image (a) gives an overview of the nanofibers network. The scale bar corresponds to 200 nm. The HRTEM micrograph in (b) shows the part of a Sb nanofiber (marked by the rectangle in Fig. 4(a)) after moderate thermal annealing at 453 K. The lattice planes as highlighted in the HRTEM image show a distance of 0.354 nm which corresponds to Sb (110) direction. The scale bar denotes 5 nm. The diffraction pattern (c) clearly shows the single crystalline nature ((110) and (120) reflections) of the nanowires after the post growth annealing at 453 K for 30 min in He atmosphere.

We assume that FIB processing with the Ga beam produces mobile Ga species on the surface which rapidly agglomerate forming catalytic nanoclusters. Sputtered Sb diffuses on the surface and acts as a quasi-vapor phase source. When the solved Sb concentration exceeds saturation, nucleation sites will be formed which initiate the precipitation of the Sb. Nanowire growth from the base continues as long as the droplet remains in a liquid state and supersaturation is maintained. At present, we do not understand the origin of the tangling of the nanowires although we note that extensive tangling has been observed previously in Ga based VLS processes [1]. The authors also stated that Ga droplets could simultaneously catalyze the growth of hundreds of thousands of nanowires.

Conclusion

In summary, the FIB irradiation of Sb with 50keV Ga ions at room temperature leads to the formation of a porous network of pure Sb nanofibers. The as-grown nanofibers are amorphous with remarkably uniform diameters in the range of about 25 nm along their entire length. The resulting porous network is uplifted several microns above the sample surface. In accordance with the catalytic VLS approach we suppose that the formation of Sb nanowires necessitates a catalytic particle, mostly a eutectic alloy, with a low melting point. Re-crystallization of the Sb nanofibers could be achieved by moderate thermal annealing at temperatures of about 473 K. Depending on the temperature ramp and heating duration finely grained crystallites as well as single crystalline regions along the nanowires can be obtained.

References

[1] Z. W. Pan, Z. R. Dai, C. Ma, Z. L. Wang, J. Am. Chem. Soc. 124, 1817 (2002).