FOCUSED ION BEAM TREATMENT OF ZnO NANOWIRES

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We investigated vapour-liquid-solid (VLS)-grown ZnO nanowires (NWs) on a Si substrate by scanning electron microscopy (SEM). Nanowires are found in a variety of shapes, surface properties and features, but seem to be all homogeneous inside. Darkish spots and areas on the surface are easily removed by a "gentle" focused ion beam (FIB) treatment. To unveil their deeper interior, we also applied FIB treatment. An overview of our results (SEM images) is given in this paper.

1. Introduction

Nanostructures have attracted much attention in recent years [1-6]. New methods have been developed to fabricate a wealth of structures [3, 4, 6-9] whose particular features depend on the precise growth conditions, substrates, and catalysis. Especially, self-assembled NWs offer a large variety of interesting and unique properties since they turned out to grow in rather excellent quality even in relatively easily controllable processes and to become nearly strain-free under these conditions. In particular, ZnO NWs have attracted renewed attention in recent years due to their peculiar optical properties [2, 6, 10-14], because this material system is a promising candidate for short wavelength optoelectronic devices. The attention to ZnO has considerably enhanced since the first report on p-doped ZnO light emitting diodes was published in 2005 [15]. Many room-temperature applications have already been shown, such as single-NW field-effect transistors, light emitting diodes, laser diodes, logic gates combining both n-type and p-type NWs, solar cells, and sensors [1, 5, 15-19]. Self-organized ZnO NWs have substantial advantages compared to other material systems, e. g., absence of surface oxidation, high exciton binding energy and ferromagnetic properties when doped with transition elements. A key property is the unique versatility in terms of geometrical dimensions and composition. However, for any application a detailed knowledge of the optical properties, their microscopic origin, surface morphology, and cross-section are of fundamental importance. In this paper, we report on investigations of the surface and cross-section of VLS-grown ZnO NWs on a Si substrate by SEM after focused ion beam (FIB) treatment. FIB systems have been produced commercially for approximately ten years, primarily for large semiconductor manufacturers; they operate in a similar fashion to a SEM except, rather than a beam of electrons, they use a finely focused beam of gallium ions for the milling of small holes into the sample at well localized sites, so that cross-sectional images of the structure can be obtained or that the structures can be polished. The applications of FIB include: cross-sectional imaging through semiconductor layered structures and devices, modification of the electrical routing on semiconductor devices, circuit modification, failure analysis, defect analysis, preparation for physical-chemical analysis, preparation of the samples for TEM of site specific locations on integrated circuits, micro-machining, mask repair, and various non-semiconductor applications.

2. Experiments

The experiments were carried out in a Dual Beam focused ion beam system (model: NOVA 200 NanoLab, company: FEI), which disposes a combined SEM/FIB chamber, at ~ $5 \cdot 10^{-7}$ mbar. For SEM imaging an acceleration high voltage of 5 kV and a beam current of 0.4 nA was used resulting in an e-beam diameter of 67.8 nm; for FIB processing, an acceleration high voltage of 30 kV and an Ga^+-ion-beam current of 1 pA and 3 nA are used, with a beam diameter of 7.0 nm and 81.0 nm, respectively. The milling time depends on area of the sample to be milled, depth, and beam energy; for the investigations in this paper we employed times from a few seconds down to fractions of a second.

The ZnO NW samples were grown on a Si substrate by the VLS-technique [20] by S. Börner in the group of Prof. W. Schade at the TU Clausthal, Germany. The geometrical structure of the obtained NWs depends strongly on the growth conditions. Temperatures at the source material and the substrate are of main influence as well as the pressure and gas flow. Due to the fact that individual wires of the as-grown ensemble cannot be directly addressed by a focused laser beam or SEM, single NWs have to be extracted from the ensemble, which was done in an ultrasonic dissolver bath, before they investigated the optical properties of ZnO single and ensemble NWs [12-14].

To be able to characterize ZnO NWs by their surface properties, SEM samples with high densities of NWs were fabricated after the procedure described above. After processing different NWs by FIB treatment the surfaces and cross-sections of the NWs were imaged by SEM.

In the following, “FIB polishing” stands for a “gentle” FIB-processing, using very short times, just to remove the top layers of the wires leaving the overall integrity undamaged, whereas “FIB milling” denotes the processing at longer exposure times not only to remove the top layers, but to drill, cut, and disintegrate the wires to gain access and insight into their interior, the overall integrity here is certainly not conserved. As the ion currents and exposure times are not unique for milling and polishing, they are explicitly given in the figures. While “polishing” normally affects the entire image area, “milling” only affects small parts of it, as can be seen by the presence of damaged regions (“craters”) in the substrate.

3. Results and discussion

3.1. SEM on as-grown NWs

Here we present the results of SEM investigations of VLS-grown ZnO NWs on a Si substrate before any FIB treatment. SEM images of ZnO NWs in Figs. 1 and 2 show that there are single NWs and ensembles of NWs, among which we found straight and bend, perfect (regular facets, smooth surfaces) and non-perfect (irregularly facetted, rough surfaces, variable widths, damaged or disintegrated) NWs, as well as NWs with clean surfaces and surfaces with dark spots and features – a property by which we categorized into Figs. 1 and 2. The sizes of the NWs are: about 2–24 μm in length and about 200–500 nm in width and height. The hexagonal facets observed emphasize the good crystalline quality of the NWs (Fig. 1).

3.2. Verifying surface features

To investigate now whether these surface specialties are propagating into the NWs, their surfaces and cross-sections have been investigated by FIB polishing (Figs. 3 and 4) and milling (Fig. 4c). Here, the removal of a prominent dark spot on a NW is nicely shown in Figs. 3a

and 3b, together with a FIB-shadow effect on the Si substrate in Fig. 3b, the NWs are not lying flatly on the ground. The cross-section of the NW at the left-hand side in Fig. 4b (arrow) is shown in Fig. 4c, with no evidence of any protrusion of the original dark spot in Fig. 4b.

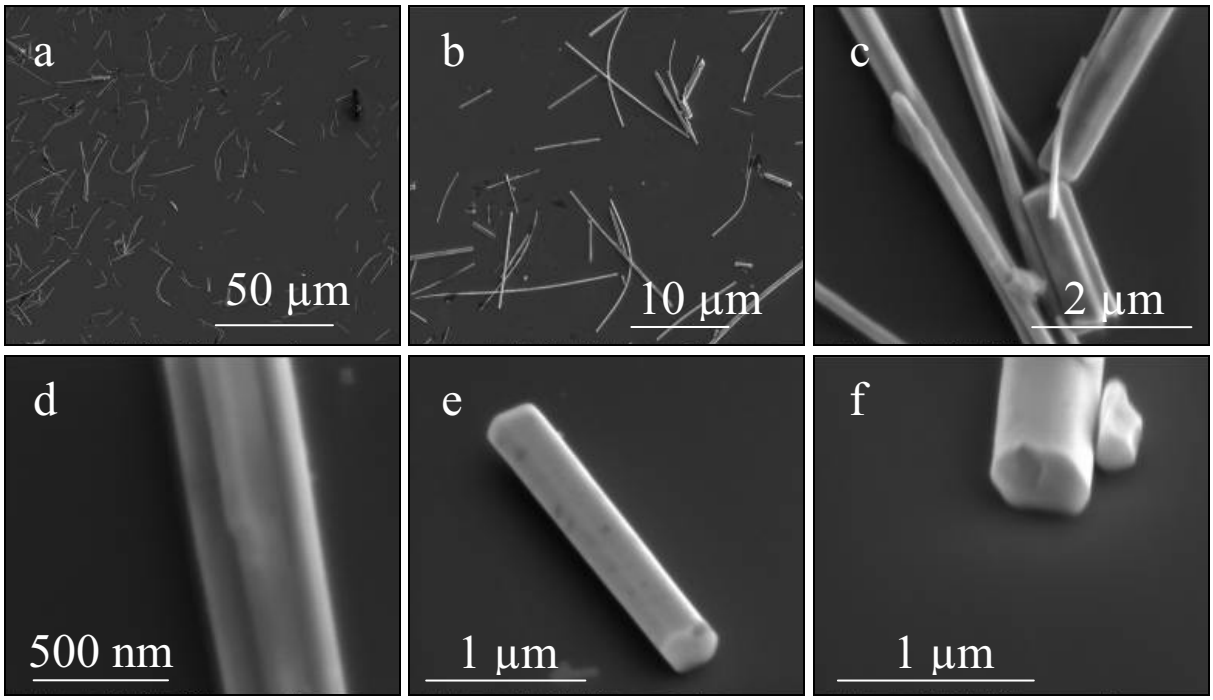

Fig. 1. SEM images of ensemble (above) and single (below) perfect ZnO NWs on Si substrate 5 kV acc. high–voltage; top view (0° tilt) in a – d, 45° tilt in e, f.

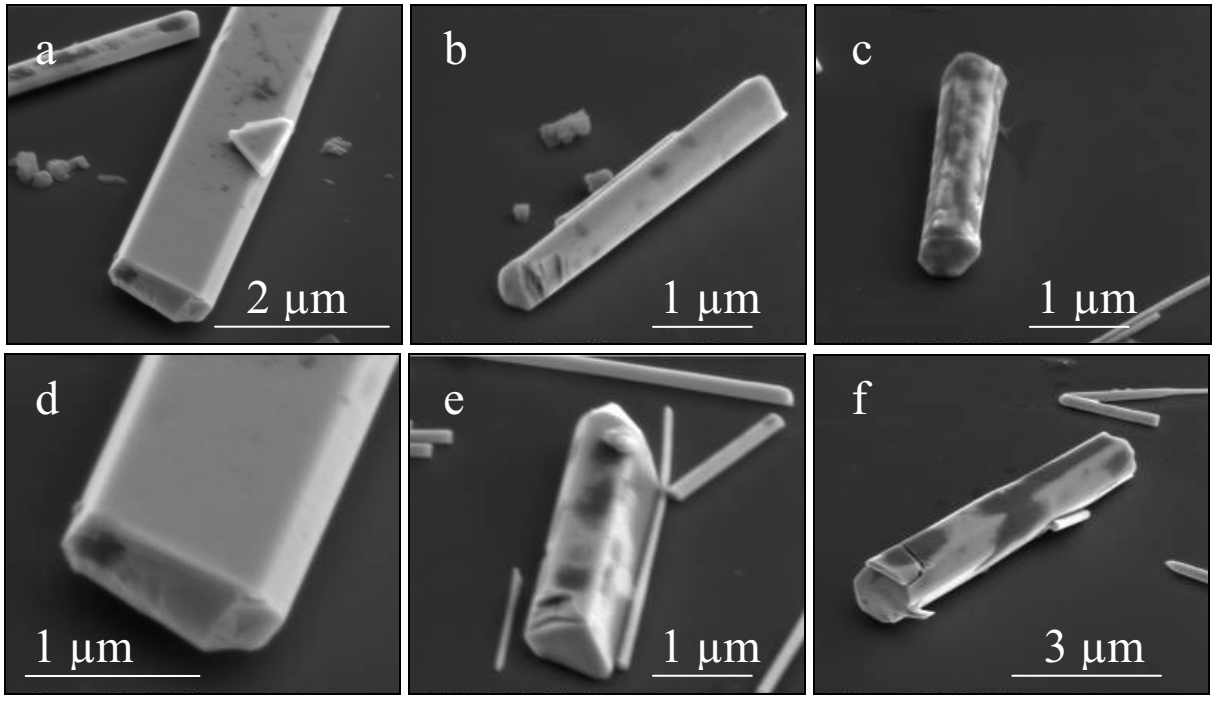

Fig. 2. SEM images of ZnO darkishly spotted single NWs on a Si substrate, image d is a zoom-in of image a; 5 kV acc. high–voltage, 45° tilt in a – f.

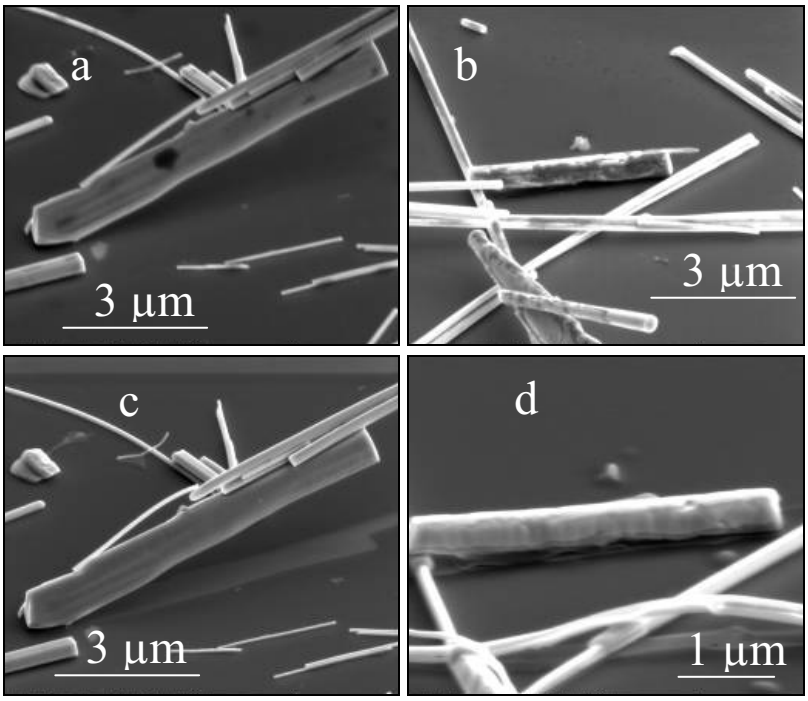

Fig. 3. SEM images of the as-prepared (a, b) ZnO NWs and after FIB polishing (c, d) at 3 nA of Ga^+ ion current for a split second; 5 kV acc. high–voltage, 52° tilt in a – d.

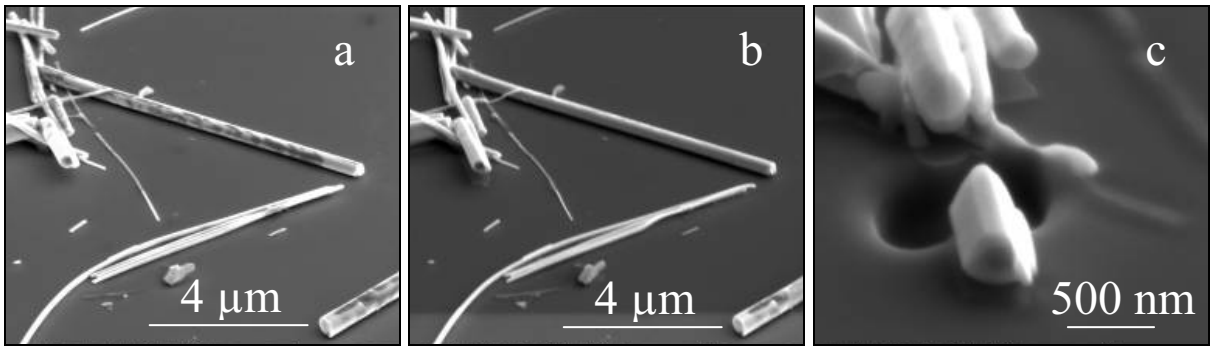

Fig. 4. SEM images of the as-prepared ZnO NWs before FIB treatment (a), after FIB polishing (b) and FIB milling (c) at 3 nA Ga^+ ion current; 5 kV acc. high–voltage, 52° tilt in a – c.

The examination of the surfaces of the NWs by SEM showed that the surface spots and features (Fig. 3, upper row) on the surfaces and facets of the NWs are removed after FIB polishing (Fig. 3, lower row), showing they are not propagating within the NWs, which is again confirmed by the cross-section image in Fig. 4c. Thus, all those dark spots and features on the NWs are real surface features. Their sizes were also measured: length ≥ 200 nm, width 5–100 nm.

3.3. Ruling out buried inhomogeneities

So, surface features are not propagating into the NWs, but what about, e.g., buried structures? For the cross-sectional investigation the NWs were again FIB milled (but with a much lower energy to "gently" thin the wires instead of a brute cut as in section 3.2), which yields information of the deeper interior of the NWs. The successive cut of a single NW (Fig. 5) again shows no evidences for any hidden inhomogeneities, an expected result as from section 3.2, but here only one wire was examined.

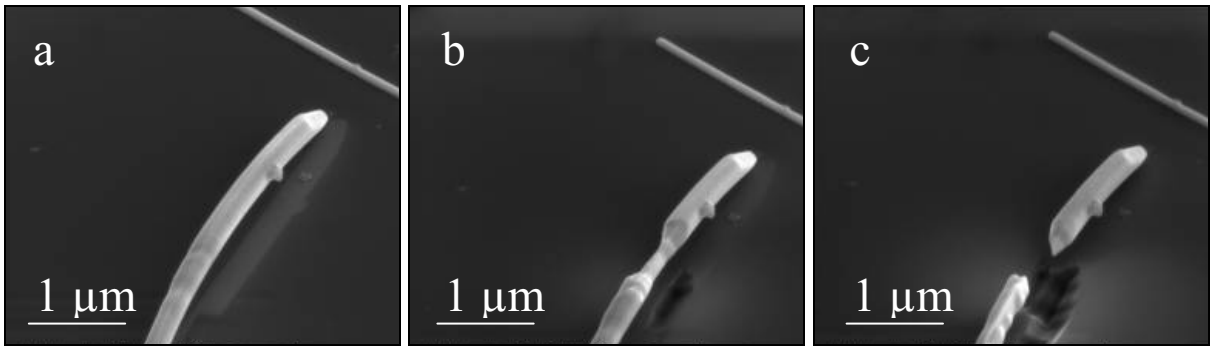

Fig. 5. SEM images of the ZnO NWs before (a) and after successive FIB milling (b and c) at 1 pA Ga^+ ion current; 5 kV acc. high–voltage, 52° tilt in a – c.

4. Conclusions

SEM investigations show that there are single and ensemble of NWs, among which we found perfect and non-perfect NWs. Surface characterization of the ZnO NWs by SEM showed that the surface of the ZnO NWs is not smooth and there are different darkish spots and features on it, which are easily removed by "gentle" FIB treatment and do not protrude into the wires. By a more "gentle" cross-sectional analysis we found out that buried structures are also totally absent. The question, how those surface features develop and if they influence the optical properties and thus show any technological relevance, remains a field of research for the future.

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