Electron Microscopy Studies of as-grown ZnO-nanorods before and after Ga-implantation in a Focused-Ion-Beam-System

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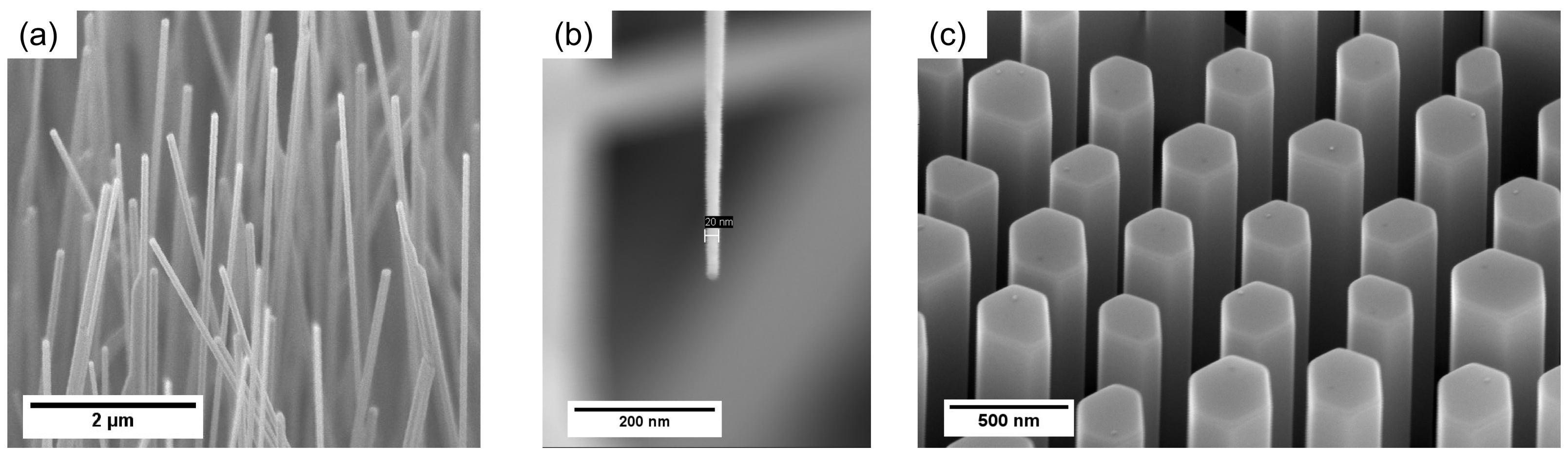
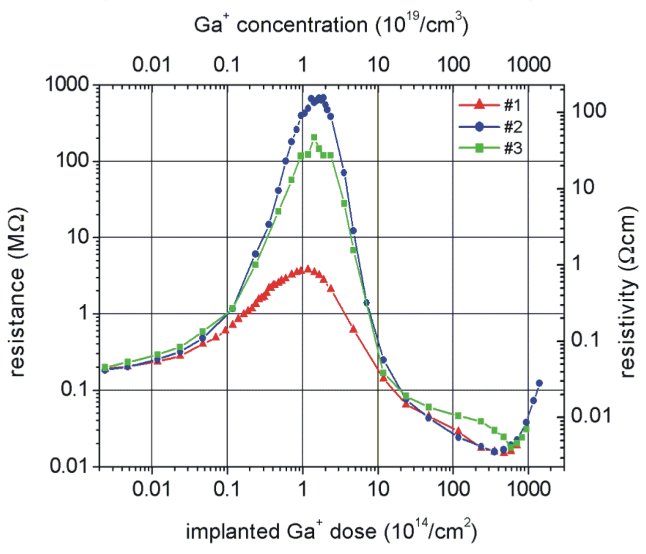
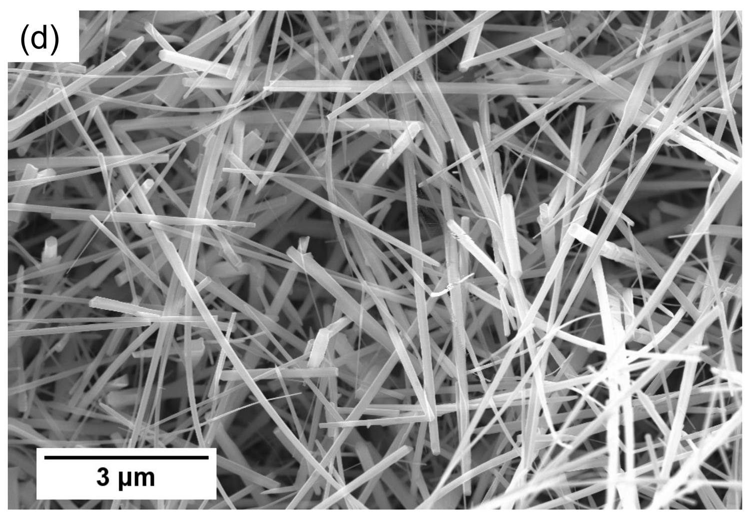
Motivation



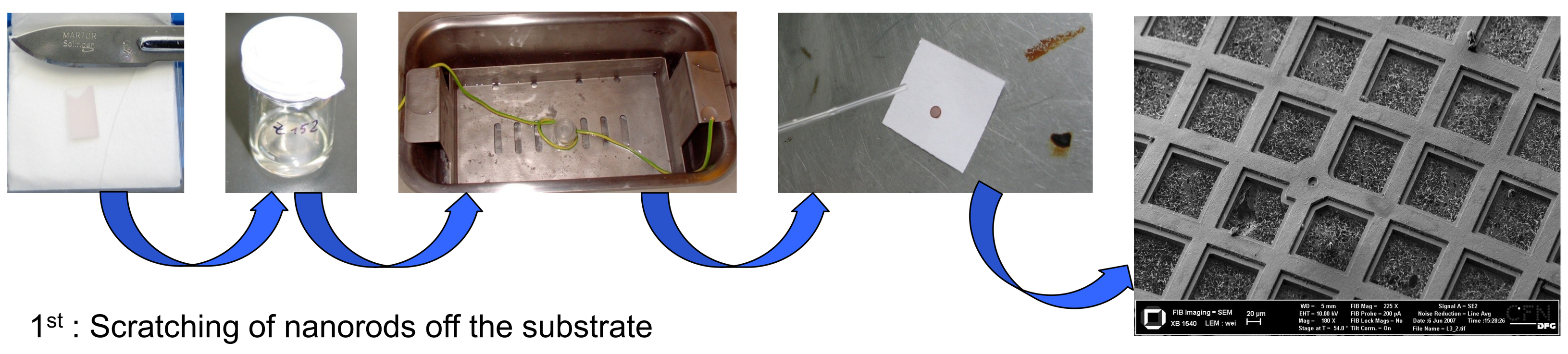
- Applications of ZnO-nanorods in (opto-)electronic devices, gas sensors, field-effect transistors
- Correlation of the structural properties with current/voltage-characteristics of single nanorods (see Weissenberger, talk HL 50.1) [1]
- High and localized doping of single nanorods by Ga^+-implantation in a focused ion beam system (FIB)
- Study of defect density and defect structure by transmission electron microscopy (TEM) before and after implantation
- Direct visualization of the electrical activity of single defects by imaging the corresponding electrical field after Ga^+-implantation by off-axis electron holography
- Study of the influence of annealing treatments on the defect structure and density





Experimental Techniques

TEM sample preparation

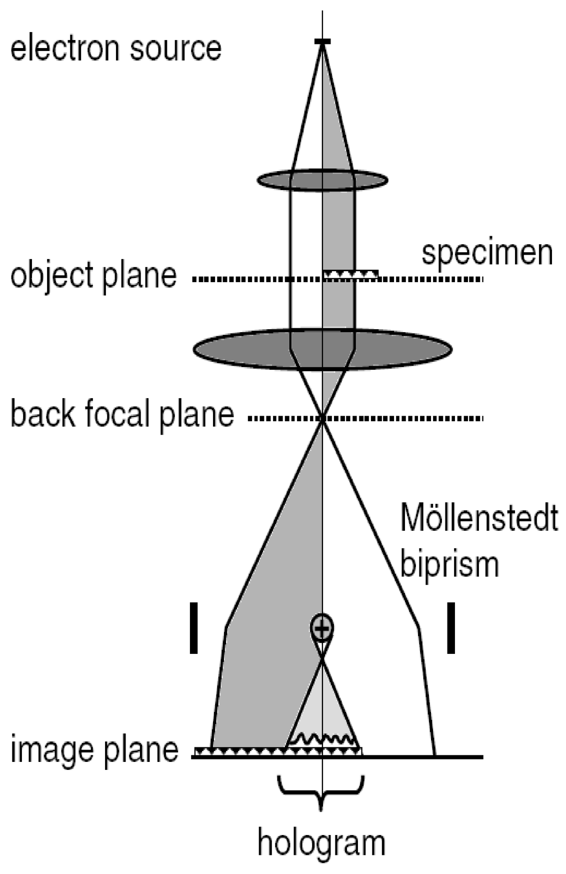


1st: Scratching of nanorods off the substrate
2nd: Dispersing of nanorods in very pure ethanol
3rd: Application of ultrasonic to reduce agglutination of the nanorods
4th: Transfer of the nanorods onto a TEM-grid on heater plate
5th: SEM image of a TEM grid with nanorods on it (check that enough nanorods were transferred and that the grid integrity is okay)
6th: Grid is ready for TEM usage

Ga^+-implantation with a FIB system 1540 EsB Crossbeam (Zeiss)

- Implantation doses $5\cdot10^{15}$ m^{-2}, $5\ 10^{16}$ m^{-2}, $5\ 10^{17}$ m^{-2}, $5\ 10^{18}$ m^{-2}, $5\ 10^{19}$ m^{-2}, $1\ 10^{20}$ m^{-2} and $1{,}5\ 10^{20}$ m^{-2} at 30 keV ion beam energy
- Destruction of TEM grid at doses > $1.5\cdot10^{20}$ m^{-2}

Transmission Electron Microscopy



- Conventional bright- and dark-field micrographs under (0002) two-beam conditions
- High-resolution TEM (HRTEM) images along the [11-20] zone axis
- Off-axis electron holography in a TEM for the reconstruction of the amplitude A(x,y) and phase φ(x,y) of the object wave function (see schematics on the left-hand side [2])

$$\psi(x,y) = A(x,y)e^{2i\pi\vec{k}\vec{r}}e^{i\varphi(x,y)}$$

- Under kinematical imaging conditions:

$$\Delta\varphi(x,y) = \sigma V_0\, t(x,y)$$

$\Delta\varphi$: phase shift of the object wave with respect to the reference wave
t: local sample thickness
V_0: mean inner Coulomb potential $V_{0,ZnO}$ = 15.5 V [4]
σ: interaction constant

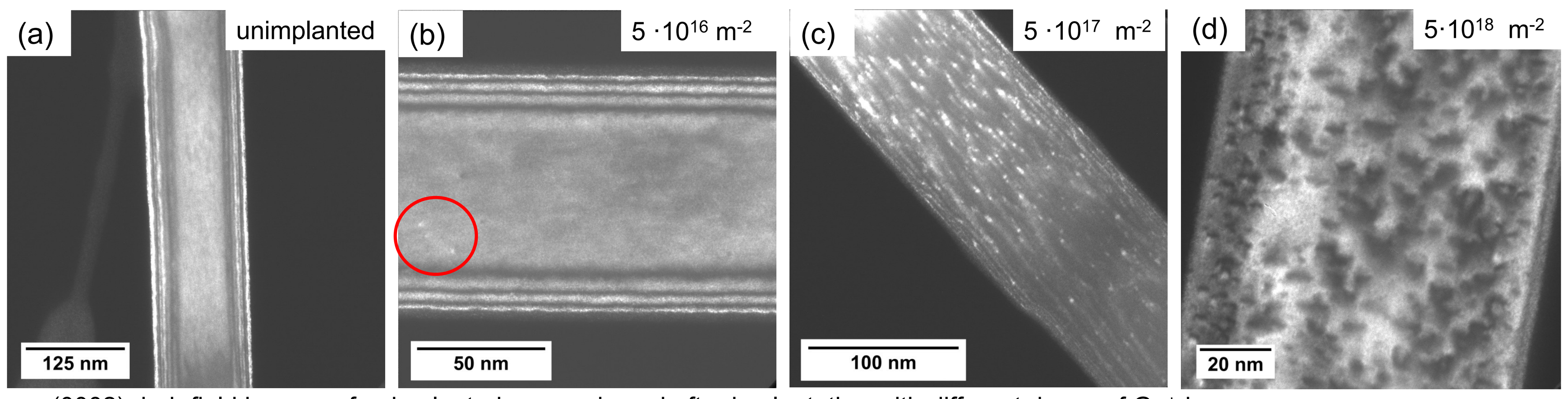
- Determination of the local nanorod thickness and nanorod shape on the basis of the reconstructed phase $\Delta\varphi$
- Detection of additional phase shifts caused by induced defects

Annealing after implantation

Goal: reduction of (point) defects and extended defects induced by implantation

- In ZnO layers: annealing at about 2/3 of the melting temperature (ZnO: ~ 2250 K) to reduce ion-induced defects [3]
- Lower temperatures expected for ZnO-nanorods due to short diffusion distances
- Annealing for 1 h from 200 °C in steps of 50 degrees up to 450 °C

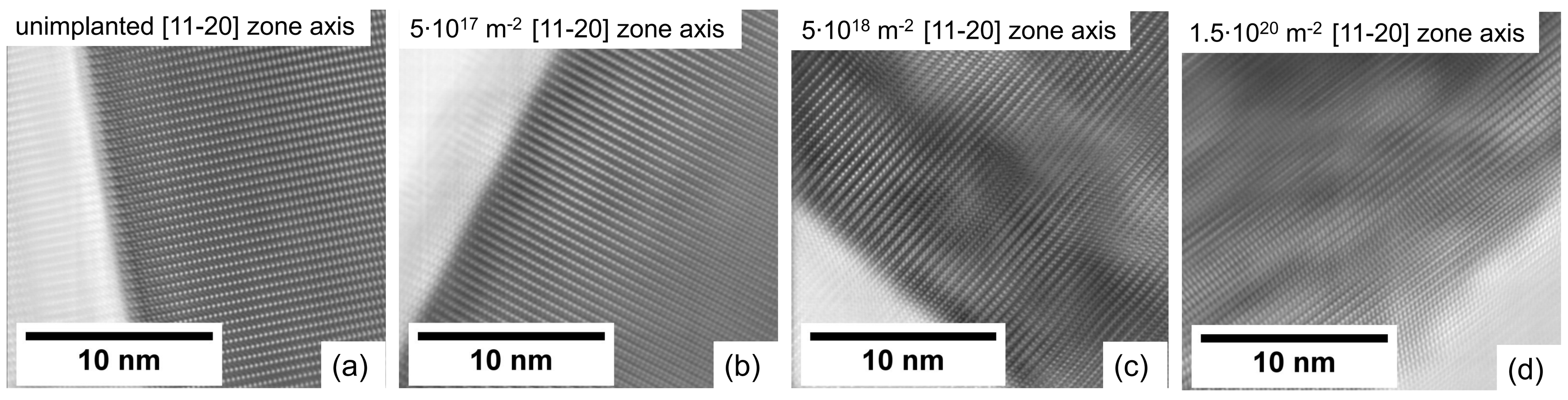
Experimental Results



(0002) dark-field images of unimplanted nanorods and after implantation with different doses of Ga^+-ions

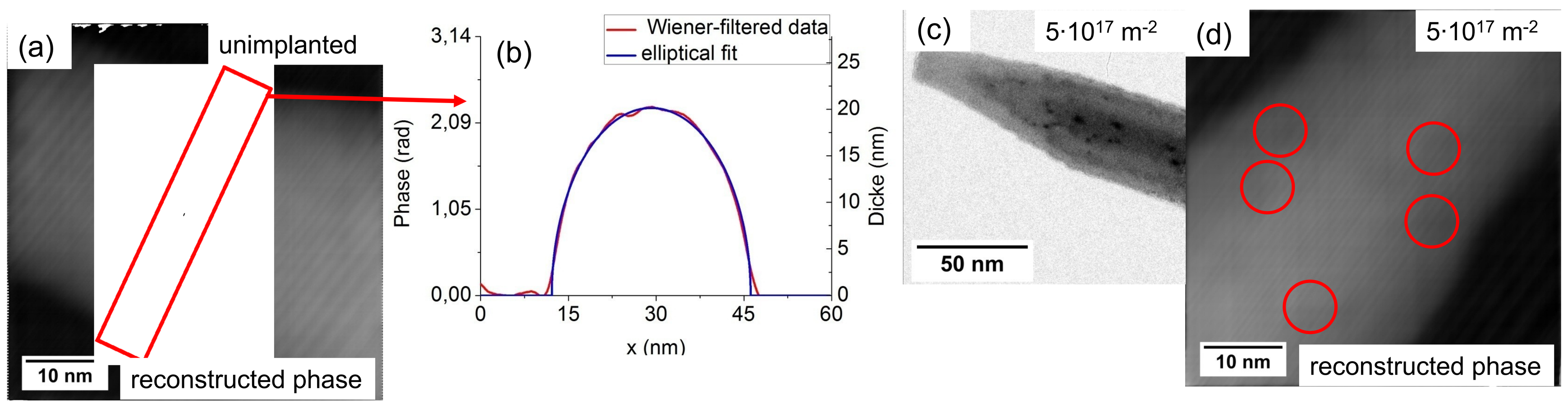
- Negligible defect concentration in as-grown nanorods (a)
- < $5\cdot10^{16}$ m^{-2} no difference between implanted and unimplanted nanorods observable
- At $5\cdot10^{16}$ m^{-2} occurrence of single localized defects (b) which increase in density and size with increasing implantation dose (c) and (d)

High Resolution Transmission Electron Microscopy



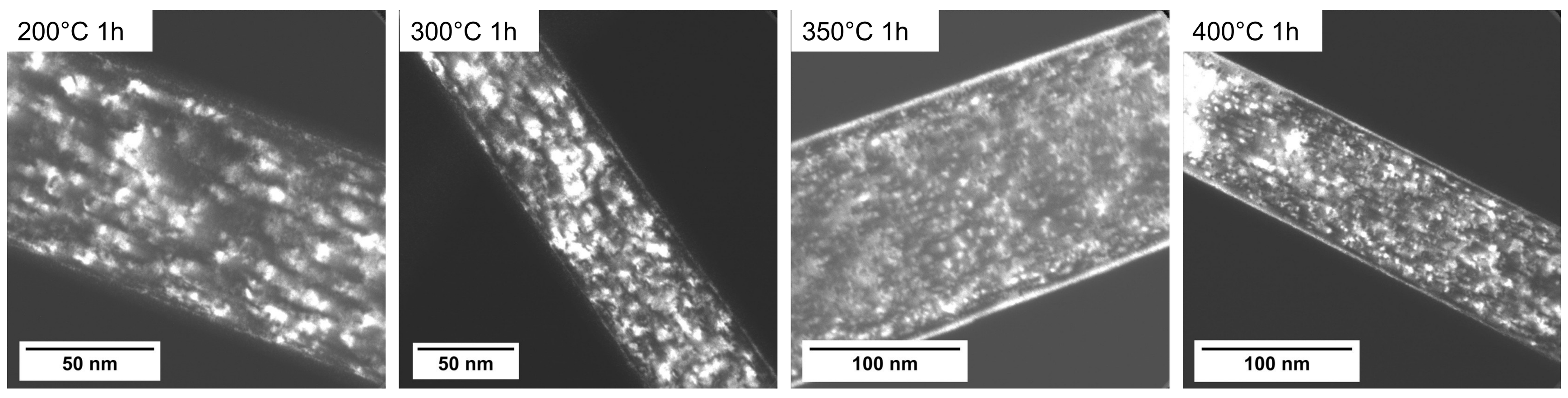
- HRTEM shows high crystalline quality of unimplanted nanorods (a)
- Regions with reduced contrast at higher implantation doses indicate an increasing concentration of point defects and extended defects (stacking faults) (c)
- Amorphization might be present at high Ga^+-implantation doses (d)

Electron Holography



- Homogeneous phase distribution along unimplanted nanorods
- Reconstruction of the three-dimensional shape of nanorods: hexagonal or elliptical cross-sections
- Observation of a phase fluctuation at a dose of $5\cdot10^{17}$ m^{-2} (d)
- Explanation: irradiation damage (thickness variation) or electrical activity of defects (c)

Annealing



(0002) dark-field images of nanorods after implantation with $5\cdot10^{18}$ m^{-2} Ga^+-ions at different annealing conditions

- No significant change in defect size and number at lower temperatures can be seen
- At higher temperatures the extension of defects regions seems to decrease

Summary

- Implantation of as-grown nanorods does not result in planar defects below $5\cdot10^{16}$ m^{-2} Ga^+-ions
- Above $5\cdot10^{16}$ m^{-2} the size and number of defects increase with increasing dose, but the lattice itself remains intact also at high implantation doses
- Difficult to find a nanorod which is parallel to the biprism
- Fluctuation of phase after implantation caused from irradiation damage or electrical activity of defects
- With annealing under argon atmosphere below 450 °C no significant change of defect density could be observed, which maybe depend on the used atmosphere

References

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