



# Structural and electrical properties of Ga-implanted ZnO nanorods

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#### **Overview**

- Ion implantation is an important doping technique in semiconductor technology which allows control of the implanted dose and selection of the implanted area.
- Disadvantage: Structural defects are generated which also strongly affect the electrical properties of the semiconductor.
- Gallium is one of the most effective shallow donor dopants for ZnO due to its low electronegativity and an ion radius similar to zinc which allows substitution on zinc lattice sites without causing significant lattice distortion [1].
- In our work, Ga<sup>+</sup> ion implantation in single ZnO nanorods is made using a focused ion beam

## Investigations on unimplanted nanorods

- Field-effect dependent measurements allow to extract the carrier mobility [4]. Typical values: 20-30 cm<sup>2</sup>/Vs or even below. An underestimate of the mobility can occur because of trapped charges in the gate insulator or at the gate insulator/nanorod interface.
- The gate voltage influences adsorption and desorption of molecules at the nanorod surface which leads to a dependence of threshold voltage and extracted carrier mobility on the chosen gate voltage range (Fig. 5a) and the sweep direction (Fig 5b,c). These effects can quantitatively vary depending on the nanorod charge. In high vacuum, the dependence of the characteristics on the gate voltage sweep direction is by far less pronounced (Fig. 5d) than under ambient conditions.
- An electron beam can be applied to desorb molecules from the nanorod surface which results in a conductivity change of more than two

(FIB) system. Electrical and structural characterization of unimplanted and implanted nanorods are performed. For the electrical characterization, they are contacted in the field-effect transistor (FET) configuration. For the structural characterization, transmission electron microscopy (TEM) is used.

### Sample preparation

- Sample growth using a vapor transport technique [2,3]
- Substrate: a-plane sapphire
- Photoluminescence (PL) shows donor-bound exciton peaks related to Ga, In and AI for nominally undoped nanorods (charge #1), which are incorporated from the source material (Fig. 2).
- For nominally In-doped nanorods (charge #2), a dominant In-related peak is visible [3]. They also contain traces of Ga and Al.





Fig.1: Scanning electron microscopy (SEM) image of a nominally undoped as-grown sample (charge #1)

- Fig. 2: PL spectrum of a nominally undoped as-grown sample (charge #1)

- orders of magnitude (Fig. 6a).
- After desorbing the molecules and blanking the electron beam, re-adsorption of some molecules takes place (Fig. 6b).







Fig. 6: (a) I<sub>ds</sub> through a single ZnO nanorod as function of electron-irradiation dose in high vacuum for  $V_{a} = 0$  V and  $V_{ds} = 1$  V. (b)  $I_{ds}$  through a single nanorod as function of time in high vacuum after turning the electron beam off for  $V_a = 0$  V and  $V_{ds} = 1$  V.

Fig. 5: (a)  $I_{ds}(V_{a})$  characteristics for different gate voltage sweep ranges under ambient conditions: -60 V to 60 V (No. 1), -40 V to 40 V (No. 2), -20 V to 20 V (No. 3) – 10 V to 10 V (No. 4). (b)  $I_{ds}(V_q)$  characteristics for both sweep directions for -10 V  $\leq V_q \leq$  + 10 V in ambient conditions for a nanorod from charge #2. The numbers indicate the sequence of the measurements and the long arrows the sweep direction. (c)  $I_{ds}(V_q)$  characteristics for both sweep directions for -10 V  $\leq V_q \leq$  + 10 V under ambient conditions for a nanorod from charge #1. The arrows indicate the sweep direction. (d)  $I_{ds}(V_q)$  characteristics for both sweep directions for -10 V  $\leq V_g \leq$  + 10 V in high vacuum. The arrows indicate the sweep direction.

### Focused Ion Beam System (FIB)

Fabrication of the TEM and FET samples:

- Scratching the nanorods from the substrate using a scalpel
- Dispersing in high-purity ethanole in an ultrasonic bath

For transmission electron microscopy (TEM) investigations, the dispersion is dropped on a TEM grid with a holey carbon film.

For transport measurements, the dispersion is dropped on a SiO<sub>2</sub>-capped Si substrate, and the contacting occurs by following steps:

- Locating of single nanorods using SEM
- Spin-coating with PMMA
- E-beam lithography at the wanted position of the contact leads, followed by developing
- E-beam evaporation of Ti/Au, followed by Lift-off
- The sample can be contacted in field-effect configuration, with the metallic leads as source and drain electrodes, and the Si substrate acting as back gate.



Fig. 3: SEM image of a single contacted nanorod under tilted view. The metallic contacts are a Ti/Au bilayer.

#### In our work, a dual beam system (ion beam/electron beam) with Ga<sup>+</sup> ions is used for ion implantation.

- The conductivity of the implanted nanorods can be measured in situ.
- The FIB system also allows local deposition of platinum from a precursor gas which is, for contacting nanorods, an alternative to the widely used E-beam lithography based procedure, and also yields ohmic contacts. Unfortunately, this technique can lead to shorting because the deposited material is not good localized.

![](_page_0_Picture_48.jpeg)

Fig. 7: The interior of the FIB system with electron column (a), ion colummn (b) and prober needles (c).

![](_page_0_Picture_50.jpeg)

Fig. 8: Nanorods contacted by FIB-induced platinum deposition with shorting (left) and without shorting (right).

#### Investigations on implanted nanorods

- Conductivity measurements as function of implanted dose show first an increase of resistance, at higher doses a decrease of resistance despite numerous extended defects which are introduced through ion implantation, as revealed by TEM investigations [5].
- TEM investigations show a complete removing of extended defects after an annealing treatment at a temperature of 700°C for implanted doses lower or equal than 5x10<sup>13</sup> cm<sup>-2</sup>.

![](_page_0_Figure_55.jpeg)

![](_page_0_Picture_56.jpeg)

Fig. 10: TEM images of ZnO nanorods: (a) unimplanted nanorod, (b) implanted nanorod with a dose of 5×10<sup>13</sup> cm<sup>-2</sup>, (c) implanted nanorod with a dose of  $5 \times 10^{13}$  cm<sup>-2</sup> after 600°C annealing treatment, (d) implanted nanorod with a dose of 5×10<sup>13</sup> cm<sup>-2</sup> after 700°C annealing treatment

#### Measurement setup

![](_page_0_Picture_59.jpeg)

A Prober module placed within a SEM specimen chamber can be used to contact microscopic contact leads (Fig. 4).

The setup can also be used for measurements within the specimen chamber of a dual beam (SEM/ Focused Ion Beam) system or under ambient air.

Fig. 4

Fig. 9: Resistance as function of implanted dose, for  $V_a = 0$ .

#### References

[1] S. Kohiki et al., J. Appl. Phys. 75, 2069 (1994) [2] A. Reiser et al., J. Appl. Phys. 101, 054319 (2007) [3] H. Zhou et al., Appl. Phys. Lett. 92, 132112 (2008) [4] W. I. Park et al., Appl. Phys. Lett. 85, 5052 (2004) [5] D. Weissenberger et al., Appl. Phys. Lett. 91, 132110 (2007)

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#### Summary

- ZnO nanorods are contacted using an E-beam lithography-based procedure. Alternatively, FIB-induced metallic depositions can be used for contacting.
- Field-effect-dependent measurements depend strongly on gate voltage sweep range and sweep direction.
- Adsorbed molecules at the nanorod surface can be desorbed by an electron beam which leads to a conductivity increase by more than two orders of magnitude.
- Ion implantation leads to a significant conductivity change as function of implanted dose.
- TEM investigations on implanted nanorods show a complete annealing of extended defects at a temperature of 700°C for implanted doses lower or equal than 5x10<sup>13</sup> cm<sup>-2</sup>.