Supporting Information

Determining the diffusion mechanisms in ZnO nanowires

ZnO nanowires synthesized via a CVD method[a] were contacted by FIB techniques (Fig.A).[b] To evaluate the mechanism of ion diffusion in their bulk, the resistance of some of these nanowires was monitored as function of the oxygen partial pressure (Fig.B) at room temperature (T = 298 K). The following experimental dependence was found in all the experiments,

$$R_{NW} \propto s^{-1} \propto p\left(O_2\right)^n \qquad \text{(i)}$$

with n = 1 / 2. This result is in agreement with reported values for ZnO single crystals,[c,d] and justified by the existence of ion diffusion based on interstitial mechanisms.[c, e] The diffusion coefficient D at T = 298 K was estimated using the formula, [f, g]

$$D(T) = \frac{L^2}{t} \qquad \text{(ii)}$$

where L is the characteristic length of the diffusion path and t the characteristic time before reaching the steady-state. For a nanowire-based sensor and a one-dimensional diffusion model, L may be the diameter F of the nanowire (see Fig.4). In figure B, the response of a ZnO nanowire with r = 110 nm (F = 220 nm) stabilizes after t = 34 h approximately. Therefore, a value of D ≈ 10^{-15} cm^2 / s is determined in agreement with reported values for the diffusion coefficient in ZnO at this temperature (10^{-15}-10^{-17} cm^2 / s).[h]

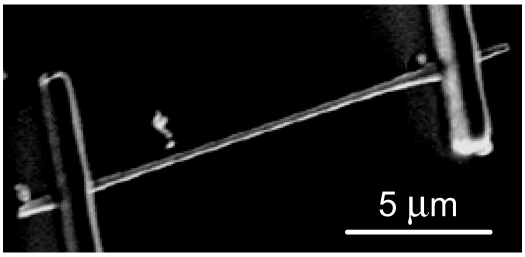

Figure A. ZnO nanowire of length L = 13 µm and radius r = 110 nm electrically contacted with FIB-techniques.

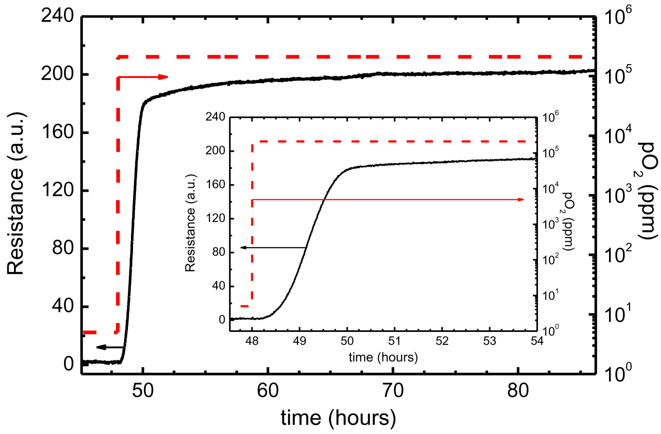

Figure B. Response of an individual ZnO nanowire (Fig.A) to a sudden change of the partial pressure of oxygen (T = 298 K). The nanowire was in low oxygen pressure for 48 hours to ensure initial stabilization. Signal stabilization to the steady-state is takes several hours. (Inset) Detail of the resistance transition from low to high oxygen partial pressure.

References

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[d] J. J. Wortman, J. W. Harrison, H. L. Honbarrier, J. Yen. “Thin Film Oxygen Partial Pressure”, NASA CR-1941, Washington, D. C. **1972.**

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[f] B. Kamp, R. Merkle, R. Lauck, J. Maier, *J. Solid State Chem*. **2005**, 178, 3027.

[g] An accurate estimation of the diffusion coefficient requires more complex studies where the Fick’s law is taken into account. For a detailed explanation see [d] and [h].

[h] J. Liu, P. Gao, W. Mai, C. Lao, Z. L. Wang, R. Tummala, *Appl. Phys. Lett*. **2006,** 89, 063125.