

Supplementary Materials: Low Temperature Vapor-Solid Growth of ZnO Nanowires for Electron Field Emission

Carina Hedrich †, Stefanie Haugg †, Leutrim Pacarizi, Robert H. Blick and Robert Zierold *

Center for Hybrid Nanostructures (CHyN), Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany

* Correspondence: robert.zierold@chyn.uni-hamburg.de; Tel.: +49-40-42838-1594

† Both authors equally contributed to the work.

Table S1. Overview of the process conditions and the nanowire dimensions including the number of nanowires analyzed.

Fig.	Temp. [°C]	mass [g]	time [h]	Ar flow [sccm]	O ₂ flow [sccm]	substrate	length [nm]	diameter [nm]	AR	N _{NW}
2a	500	0.7	4	50	25	SiO ₂ /Si	no NW formation			
2b	550	0.7	4	50	25	SiO ₂ /Si	570 ± 64	171 ± 28	3.3	12
2c	580	0.7	4	50	25	SiO ₂ /Si	543 ± 56	186 ± 43	2.9	11
2d	620	0.7	4	50	25	SiO ₂ /Si	233 ± 64	101 ± 25	2.3	13
2e	650	0.7	4	50	25	SiO ₂ /Si	78 ± 28	86 ± 31	0.9	10
3a	550	0.7	4	50	25	SiO ₂ /Si	104 ± 34	67 ± 12	1.6	17
3b	550	0.7	4	50	25	SiO ₂ /Si	no NW formation			
3c	550	0.7	4	50	25	SiO ₂ /Si	no NW formation			
4a	580	0.7	4	50	25	SiO ₂ /Si	543 ± 56	186 ± 43	2.9	11
4b	580	0.7	4	50	50	SiO ₂ /Si	357 ± 57	186 ± 27	1.9	14
4c	580	0.7	4	50	83	SiO ₂ /Si	646 ± 41	227 ± 55	2.8	12
5a	580	0.7	2	100	83	SiO ₂ /Si	600 ± 55	180 ± 40	3.3	19
5b	580	0.7	4	100	83	SiO ₂ /Si	646 ± 41	227 ± 55	2.8	12
5c	580	0.7	8	100	83	SiO ₂ /Si	697 ± 79	231 ± 48	3.0	14
5d	580	0.7	8	100	83	SiO ₂ /Si	697 ± 79	231 ± 48	3.0	14
5e	580	1.4	4	100	83	SiO ₂ /Si	1355 ± 329	243 ± 72	5.6	17
5f	580	2.8	4	100	83	SiO ₂ /Si	2014 ± 550	524 ± 109	3.8	17
5g	580	1.4	8	100	83	SiO ₂ /Si	1270 ± 110	461 ± 171	2.8	11
5h	580	3.5	1	100	83	SiO ₂ /Si	466 ± 72	175 ± 59	2.7	16
5i	580	3.5	4	100	83	SiO ₂ /Si	3290 ± 854	401 ± 65	8.2	12
5j	580	3.5	8	100	83	SiO ₂ /Si	4753 ± 1272	599 ± 101	7.9	13
5k	580	3.5	12	100	83	SiO ₂ /Si	5196 ± 1144	484 ± 112	10.7	13
5l	580	3.5	16	100	83	SiO ₂ /Si	6861 ± 1503	429 ± 113	16.0	17
7a	580	1.4	4	100	83	SiO ₂ /Si	1355 ± 329	243 ± 72	5.6	17
7b	580	1.4	4	100	83	Si ₃ N ₄	1385 ± 72	236 ± 59	5.9	11
7c	580	1.4	4	100	83	n-doped Si	863 ± 191	347 ± 77	2.5	17
7c	580	1.4	4	100	83	n-doped Si	903 ± 173	361 ± 76	2.5	57
7d	580	1.4	4	100	83	Ti/Si	1080 ± 370	389 ± 86	2.8	17
7e	580	0.7	4	50	25	ZnO/ SiO ₂ /Si	no NW formation			
7f	580	0.7	4	50	25	AuNP/ SiO ₂ /Si	no NW formation			
8a	580	3.5	20	100	83	n-doped Si	4871 ± 809	344 ± 115	14.2	11
8b	580	3.5	20	100	83	Ti/Si	4392 ± 596	406 ± 255	10.8	10
8c	580	3.5	20	100	83	Ti/SiN membrane	2937 ± 493	381 ± 224	7.7	10
S2	580	3.5	20	100	83	SiO ₂ /n-doped Si	8216 ± 1340	721 ± 81	11.4	13

Argon flow

Varying the argon flow does not influence the morphology of the ZnO nanowires as much as the variation of the oxygen flow. The argon flow was varied between 25 and 138 sccm.

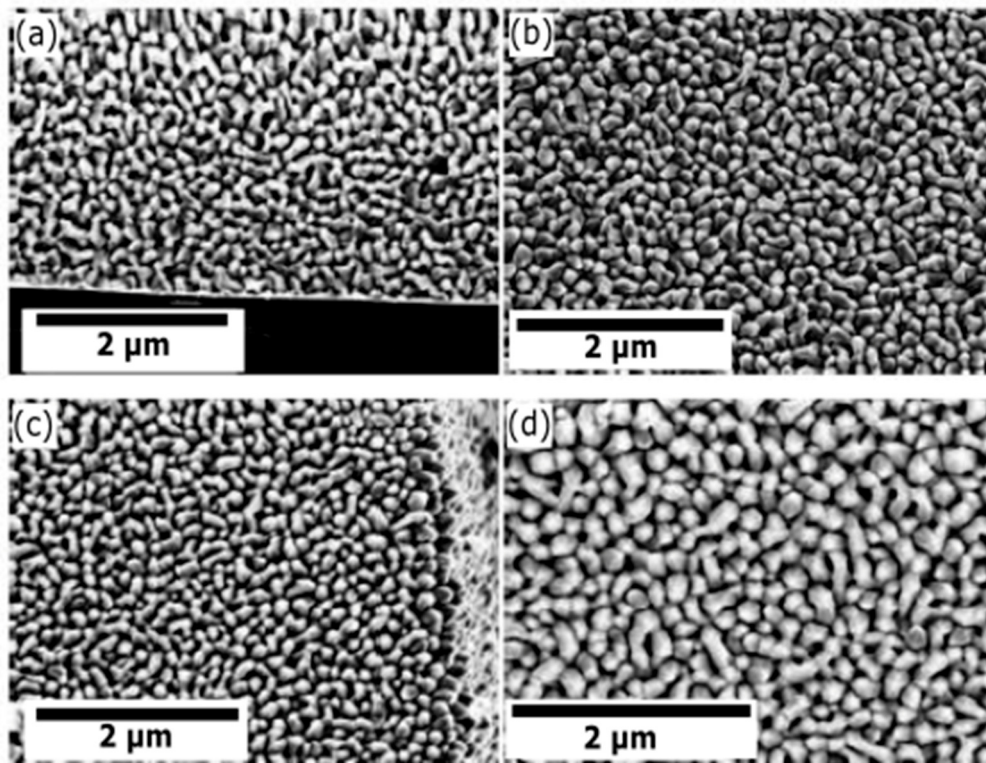


Figure S1. Scanning electron microscope images showing the morphology of ZnO nanowires grown at different argon flows. The used argon flow was (a) 25 sccm, (b) 50 sccm and (c) 100 sccm and (d) 138 sccm. Nanowires grew at all samples and the morphologies of the wires and their surface facets and tips are similar.

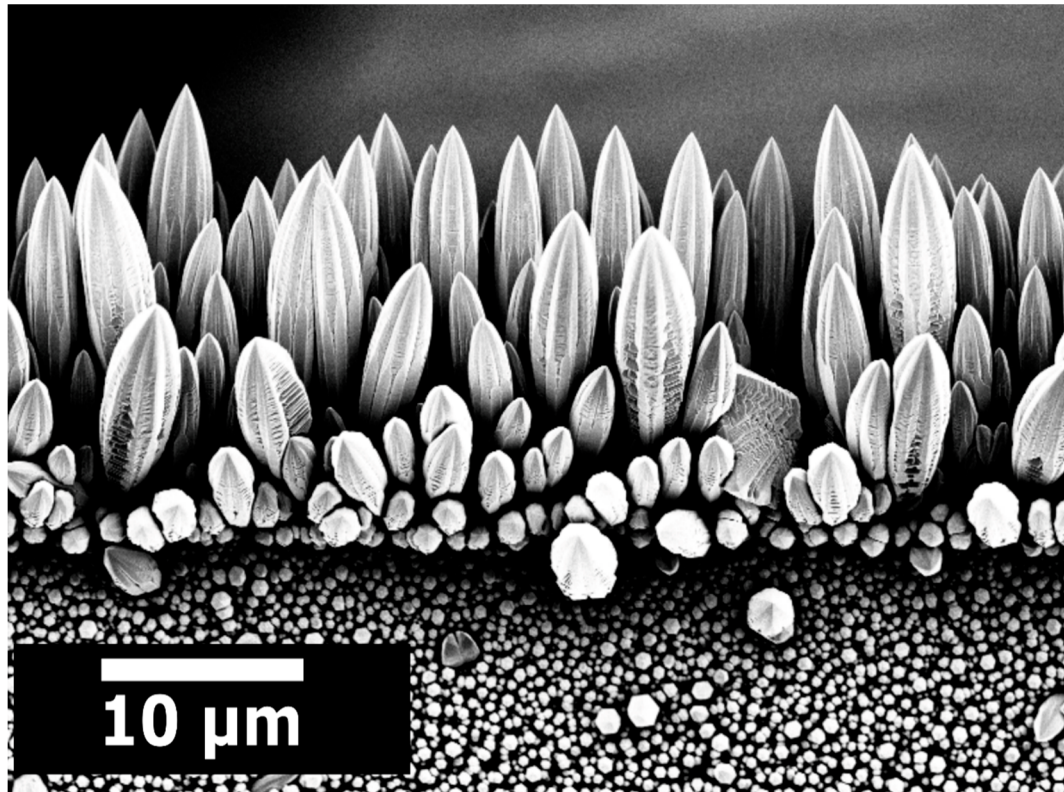


Figure S2. SEM picture of ZnO nanowires produced by using a Zn precursor amount of 3.5 g and a growth temperature of 20 h.

Theoretical calculation of field emission current

According to the Fowler-Nordheim theory for electron field emission, the relation of the emission current I and the macroscopic applied electric field F_M can be written as:

$$I = a_{FN} \cdot A_{em} \cdot \frac{(\gamma F_M)^2}{\phi} \exp\left(-\frac{b_{FN} \phi^{3/2}}{\gamma F_M}\right) . \quad (1)$$

with $a_{FN} \approx 1.5414 [\mu A][eV][V]^{-2}$ and $b_{FN} \approx 6.83089 [eV]^{-3/2}[V][nm]^{-1}$ being the Fowler-Nordheim field emission parameters I and II, respectively [45]. For theoretical calculation of the applied electric field that would be necessary to cause a current in the picoampere range from ZnO emitters, an emission area of $A_{em} = 4 \text{ mm}^2$ (size of the opening in the PTFE sheet, separating sample and grid electrode) and a work function of $\phi = 5.3 \text{ eV}$ for ZnO were taken into account [46]. As geometrical field enhancement factor γ —describing the ratio of the local electric field on the emitter's surface to the macroscopic applied electric field—a value of $\gamma_{flat} = 1$ was used to simulate a perfectly flat ZnO film. A factor of $\gamma_{nanowires} = 58$ was applied for ZnO nanowires, as it was derived from the experimental field emission data from the ZnO nanowires grown on n-doped Si (Figure 8).

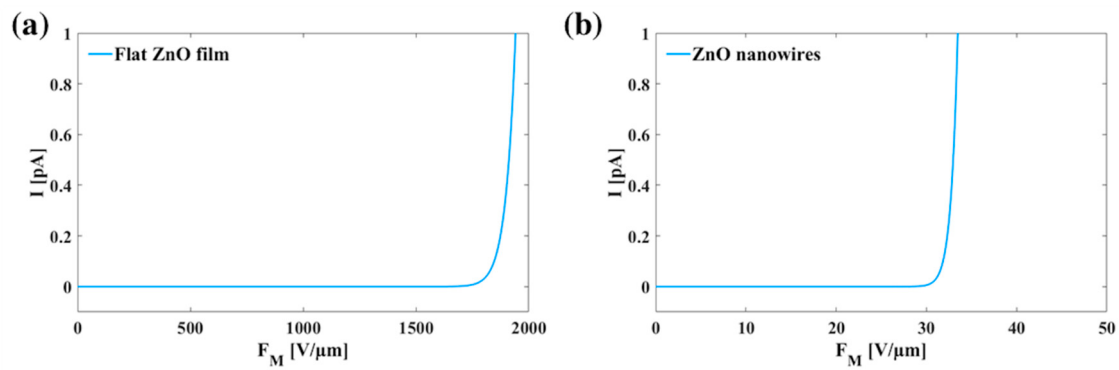


Figure S3. Field emission current over applied electric field for (a) perfectly flat ZnO film and (b) ZnO nanowires. The applied electric field that is necessary to cause electron emission via field emission can tremendously be lowered by the geometrical field enhancement effect [45].