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Supporting Information

Cold Field Electron Emission of Large-area Arrays of SiC Nanowires: Spatial Analysis,

Photo-Enhancement and Saturation Effects.

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Fig. S1 Nickel mounds after melting and dewetting of the surface, before SiC NWs growth.



Fig. S2 STEM-HAADF overview of single SiC NWs. The presence of the catalyst on the tip of the nanowires is an evidence of the VLS float growth ^{S1} and a confirmation comes from the tapered shape of the wires: the cause of that can be the radial growth at the base or the catalyst consumption during the growth ^{S2}.

Fowler-Nordheim Theory for Metals

According to standard FN theory, ¹ the FE current density for a flat, clean metal surface is described by

$$J = \frac{A}{\varphi} E_0^2 \exp\left(-\frac{B\varphi^3}{E_0}\right) (S1)$$

set that $E_0 = V/d$ is the applied field, V is the applied voltage, d is the inter-electrodes gap, φ is the work function of the electron-emitting material, $A = 1.54 \cdot 10^{-6} \text{ eV/V}^2$ and $B = 6.83 \cdot 10^3 \text{ V} \cdot \text{eV}^{3/2}/\mu\text{m}$ are constants. Equation (S1) is a 1-dimensional approximation which gives a correct description of experimental FE current densities from 0 K up to room temperature. Equation (1) holds for ideally smooth metal surfaces, but it still describes correctly CFE currents from real emitters decorated by a superficial micro-roughness provided that the electric field is now expressed by $E = \beta V/d = \beta E_0$, β being the so-called "field enhancement factor". Equation (S1) can then be rearranged in the following way

$$\ln\left(\frac{I}{E_0^2}\right) = \ln\left(\frac{A}{\varphi} \cdot \beta^2 \cdot area\right) - \frac{B\varphi^{\frac{3}{2}}}{\beta} \cdot \frac{1}{E_0} (S2)$$

where *area* is the effective emitting area. In fact, experimental data show that FE currents do not originate from the whole surface of metallic macro-cathodes, but they are restricted to the micron-sized protrusions constituting the surface roughness.

CFE from LAFE systems

The emission current from LAFE systems comes, actually, only from a limited fraction of the total substrate area. To take this into account it has been introduced ⁶⁴ the parameter "area efficiency of emission" α , defined as the ratio between the so-called "notional emission area" A_n and the "macroscopic area" or total area of the substrate A_M . A_n is defined according to ⁶⁴

$$I = \int_{A_M} J_L dA = J_0 A_n \quad (S3)$$

provided that *I* is the total current from an emitter of macroscopic area A_M , J_L is the local CFE current density dependent on position over the emitter surface, and J_0 is the maximum local CFE current density, where the label 0 refers to the position on the emitting surface at which J_L is highest at the given applied voltage.

Table S1 Review of CFE of SiC nanostructures under dark conditions.

1D field emitters	Threshold field, E_{Th} [V / μ m]	Turn-on field, <i>E_{TO}</i> [V / μm]	References
SiC NWs on a silicon synthesized by hot-filament- assisted CVD with a solid silicon and carbon source.	30 at a current density of 10 mA/cm ²	20	Wong et al. ³³
FE meausrements at pr	essure of about $5 \cdot 10^{-1}$	³ Torr	
Bunches of SiC NWs grown by SiC and Fe powders through heating.	8.5	5	Wu et al. ³⁴
FE meausrements at pr	essure of about 10^{-10}	Torr.	
Core–shell SiC–SiO ₂ NWs synthesized by direct heating the NiO-coated silicon substrate under reductive environment by the carbothermal reduction of WO ₃ by C; thickness of SiO ₂ was varied through HF-etching.	-	4.0 (bare SiC NWs), 3.3 (10 nm SiO ₂ - coated SiC NWs) and 4.5 (20 nm SiO ₂ -coated SiC NWs).	Ryu et al. ³⁵
FE meausrements at pre	essure of about $1 \cdot 10^{-4}$	Torr.	
SiC NWs grown from the surface of SiC bulk ceramic substrate by catalyst-assisted thermal heating.	5.77	3.33	Deng et al. ³⁶
FE meausrements at p	ressure of about 10 ⁻⁸	Torr.	
.β-SiC NWS obtained by thermal evaporation of SiO powders onto activated C fibers.	-	3.1 - 3.5	Zhou et al. ³⁷
FE meausrements a	at pressure of $3 \cdot 10^{-5}$ P	a.	
Ga-catalyzed VLS-grown bamboo-like β-SiC NWs; highly faceted hexagonal cross-sections and sharp corners.	_	10	Shen et al. ³⁸
	essure of about $5 \cdot 10^{-7}$	Torr.	
FE meausrements at pre			T

1D field emitters	Threshold field, E_{Th} [V / μ m]	Turn-on field, <i>E_{TO}</i> [V / μm]	References
VS-grown SiC nanowires arrays on Si substrate.	10.5 (aligned NWs); 29.5 (random oriented NWs)	14 (aligned NWs); 37 (random oriented NWs)	Niu et al. ⁴⁰
FE meausrem	nents at pressure of about 5.	10 ⁻⁵ Pa.	
MOCVD-grown β-SiC NWs.	2 (for $I_{Th} = 5$ nA, corresponding to a current density of 0.025 μ A/cm ² ;	-	Kim et al. ⁴¹
FE meausrements at pressu	are of about 10^{-7} Torr; $\beta(\varphi(S))$	SiC) = 5 eV) = 2000.	
Microwave assisted vapor-solid-grown ultrathin 3C–SiC nanobelts.	-	3.2	Wei et al. 42
FE meausrem	nents at pressure of about 4.	10 ⁻⁷ Pa.	
Porous SiC NWs obtained through carbonizing of metal-assisted chemically etched silicon NWs.	-	Dependent on the anode-cathode distance d: 2.9, 2.6 and 2.3 for $d= 300, 400 and 500 µm$	Yang et al. ⁴
FE meausrements at pressur	e of about $2 \cdot 10^{-4}$ Pa; $\beta(\varphi(Si))$	C) = 4.53 eV) = 5241 .	
Catalyst-free tubular β -SiC nanostructures.	10 at a current density of 10 mA/cm ²	< 5	Cui et al. 44
The pressure at wh	ich FE were performed was	not reported.	
β-SiC NWs Felted NWs (catalyst-free on graphite substrate), curly NWs (catalyst-free on Si substrate), styraight NWs (Ni-catalyzed on graphite substrate).	5.3 (felted NWs) / 3.25 (curly NWs) / 2 (straight NWs)	2 (felted NWs) / 1.5 (curly NWs) / 1 (staright NWs); at a current density of 10 mA/cm ²	Li et al. ⁴⁵
FE meausrem	nents at pressure of about 10	- ⁸ Torr.	
Al-doped 3C-SiC (bunch-like) NWs.	1.38 - 1.54	0.55 - 0.85	Zhang et al. ⁵

1D field emitters	Threshold field, E_{Th} [V / μ m]	Turn-on field, <i>E_{TO}</i> [V / μm]	References
Al2O3 decorated and bare tubular β-SiC (bunch-like) nanostructures.	$\begin{array}{c} 23.5 \text{ (bare } \beta \text{-SiC} \\ \text{nanostructures)} / 5.37 \\ \text{(Al2O3 decorated } \beta \text{-SiC} \\ \text{nanostructures)} \text{ at a} \\ \text{current density of 10} \\ \text{mA/cm}^2 \end{array}$	8.8 (bare β-SiC nanostructures) / 2.4 (Al2O3 decorated β- SiC nanostructures)	Cui et al. ⁴⁶
The pressure at wh	ich FE were performed was 1	not reported.	
Lawn-like 3C-SiC NWs; hexagonal cross section; presence of microtwins and SFs.	-	2.1	Chen et al. 47
FE meausrements at pressure	e of about $5 \cdot 10^{-5}$ Torr; report	of two linear regimes	
3C-SiC nanoneedles synthesized by catalyst- assisted pyrolysis of polyaluminasilazane precursors; concentration of $Al = 0.7$ %.	-	1.3 (RT)	Wei et al. ^{S4}
FE meausrements at pressure o	f about $5 \cdot 10^{-7}$ Pa; range of te	mperature: RT – 500 °C.	
Two-step VS-grown β -SiC nanobelts with a median ridge (NW with two lateral flakes); presence of SFs.	-	3.2	Meng et al. St
FE meausren	nents at pressure of about 10	⁻⁷ Torr.	
CVD-grown nonaligned-SiC NWs on Si nanoporous pillar array; presence of SFs.	-	2.9	Wang et al. So
FE meausrements at p	ressure of about $2 \cdot 10^{-7}$ Pa; φ	(SiC) = 4.4 eV.	
1,10-phenanthroline- assisted molecule template β-SiC NWs; presence of SFs.	8.12	3.57	Xi et al. ^{S7}
The pressure at wh	ich FE were performed was 1	not reported.	
Fe-assisted VLS-grown β-SiC NWs on flexible carbon fabric; hexagonal cross section; presence of microtwins and SFs.	-	1.2	Wu et al. ^{S8}

CFE from SiC nanostructures under dark conditions					
1D field emitters	Threshold field, E_{Th} [V / μ m]	Turn-on field, <i>E_{TO}</i> [V / μm]	References		
N-doped quasialigned 3C-SiC NWs via the pyrolysis of polymeric precursor with Co(NO3)2 as the catalyst; concentration of N = 2.38 %; presence of SFs.	2.53–3.51;	1.90–2.65	Chen et al. ^{S9}		
FE meausrements at pressure of about $3 \cdot 10^{-7}$ Pa; $\beta(\varphi(SiC) = 4.0 \text{ eV}) = 1710$.					
CVD-grown 3C-SiC nanoneedles synthesized on carbon cloth; presence of SFs.	2.2	1.3	Wu et al. ^{S10}		
FE meausrements at pressure of about 5.10 ⁻⁵ Pa; $\beta(\varphi(SiC) = 4.0 \text{ eV}) = 3667$.					
3C-SiC nanoneedles on highly flexible carbon fabric via the catalyst assisted pyrolysis of polysilazane; presence of SFs and twins.	2.2 (undoped nanoneedles); 1.7 – 2 (N- doped nanoneedles; concentration of N = 3 %)	1.6 (undoped nanoneedles); 1.1 - 1.35 (N-doped nanoneedles; concentration of N = 3 %)	Zhang et al.		
CVD-grown 3C-SiC nanoneedles synthesized on carbon cloth; presence of SFs.					
Quasialigned SiC nanoarrays with sharp tips via catalyst assisted pyrolysis of polymeric precursors on carbon fabric; concentration of N = 3.35 %; presence of SFs.	-	2.19 – 1.15	Chen et al. ^{S12}		

FE meausrements at pressure of about $1.5 \cdot 10^{-7}$ Pa.

H_2 and N_2 plasma-treated β -SiC NWs.	6.7 (10 minutes of H ₂ -	3.2 (10 minutes of H ₂ -	Li et al. ^{S13}
	treatment); 6.3 (20	treatment); 3.0 (20	
	minutes of H ₂ -treatment);	minutes of H ₂ -	
	6.0 (10 minutes of N ₂ -	treatment); 2.8 (10	Li et al.
	treatment); at a current	minutes of N ₂ -	
	density of 10 mA/cm ²	treatment)	

FE meausrements at pressure of about 10⁻⁷ Torr.

1D field emitters	Threshold field, E_{Th} [V / μ m]	Turn-on field, <i>E_{TO}</i> [V / μm]	References
B-doped 3C-SiC nanowires via catalyst assisted pyrolysis of polymeric precursor; triangular prism-like body. B-doped NWs: concentration of B = 5.03 %, density of $1.3 \cdot 10^{-6}$ NW/cm ² , very rough sidewalls and presence of SFs; undoped NWs: $2.3 \cdot 10^{-6}$ NW/cm ² and smoother sidewalls.	1.7 (B-doped nanoneedles)	1.35 (B-doped nanoneedles)	Yang et al. ^{S1.}
FE meausrements at pressur	e of about $3 \cdot 10^{-7}$ Pa; β (φ (Si	C) = 4.0 eV) = 4895.	
N-doped SiC nanoneedles via catalyst-assisted pyrolysisof polysilazane precursor, on carbon fabrics.	1.79 (concentration of N = 4.39 %), 1.64 (concentration of N = 6.01 %), 1.55 (concentration of N = 7.58 %)	1.38 (concentration of N = 4.39 %), 1.22 (concentration of N = 6.01 %), 1.11 (concentration of N = 7.58 %)	Chen et al. ^{S15}
FE meausrements at pro	essure of about $1.5 \cdot 10^{-7}$ Pa; of	p(SiC) = 4.0 eV.	
n-type SiC NWs via Au-assisted pyrolysis of polyureasilazane on 6H-SiC wafer substrates; concentration of N = 3.01 %; density of $5.7 \cdot 10^7$ NWs / cm ² .	2.65 (RT); 1.33 (500°C)	1.50 (RT); 0.94 (500°C)	Wang et al.
FE meausrements at pressure of about $1.5 \cdot 10^{-7}$	Pa; range of temperature: R' 4482.	$\Gamma - 500$ °C; β (ϕ (SiC) = -	4.0 eV; RT) =
n-type SiC NWs via Au-assisted pyrolysis of polyureasilazane on 6H-SiC wafer substrates; concentration of N = 3.01 %; density of $5.7 \cdot 10^7$ NWs / cm ² .	2.69 (2.9·10 ⁷ NWs / cm ²); 2.34 (4.0·10 ⁷ NWs / cm ²); 2.96 (5.7·10 ⁷ NWs / cm ²);	1.79 (2.9·10 ⁷ NWs / cm ²); 1.57(4.0·10 ⁷ NWs / cm ²); 1.95 (5.7·10 ⁷ NWs / cm ²)	Wang et al.
FE meausrements at pressure of about $1.5 \cdot 10^{-7}$ cm ²) = 334		10^7 NWs / cm ²) = 3300, β	(4.0·10 ⁷ NWs /
B-doped SiC NWs via the catalyst-assisted pyrolysis of polyborosilazanes on 6H-SiC wafer substrates; concentration of $B = 5.3$ %; density of $3.9 \cdot 10^7$ NWs / cm ² .	3.21 (RT); 1.33 (500°C)	1.92 (RT); 0.98 (500 °C)	Wang et al.
FE meausrements at pressure of about $2.0 \cdot 10^{-7}$	Pa; range of temperature: R7	$\Gamma - 500 ^{\circ}\text{C}; \beta(\phi(\text{SiC}) = 4.$	(0 eV) = 3643.
N-doped SiC nanoneedles via catalyst-assisted pyrolysis of polysilazane precursor, on carbon fabrics; concentration of N = 2.75 %.	-	1.58 (RT); 0.65 (500 °C)	Ying et al. ^{S19}

CFE from SiC nanostructures under dark conditions			
1D field emitters	Threshold field, E_{Th} [V / μ m]	Turn-on field, <i>E_{TO}</i> [V / μm]	References
Undoped and N-doped SiC nanoneedles.	6.9 (undoped nanoneedles), 5.6 (concentration of N = 0.975 %), 4 (concentration of N = 1.336 %), 6.3 (concentration of N = 2.265 %)	2.9 (undoped nanoneedles), 1.9 (concentration of N = 0.975 %), 1.5 (concentration of N = 1.336 %), 2.1 (concentration of N = 2.265 %)	Zhao et al. ^{S20}

FE meausrements at pressure of about 10^{-8} Torr.

Bare and Au-decorated SiC NWs grown via pyrolysis of polysilazane precursor, on carbon fabrics.	2.75 (bare NWs), 1.75 (Au-decorated NWs)	2.1 (bare NWs), 1 (Au- decorated NWs)	Chen et al. ^{S21}	
FE meausrements at pressure of about $1.5 \cdot 10^{-7}$ Pa; $\varphi(SiC) = 4.0 \text{ eV}$: $\beta(bare NWs) = 1150$, $\beta(Au-decorated NWs) = 6244$.				
Gourd-shaped N-doped 4H-SiC NWs via an electrochemical anodic oxidation process; concentration of $N = 2.75$ %.	-	0.95 (RT)	Chen et al. ^{S22}	
FE meausrements at pressure of about $1.5 \cdot 10^{-7}$ Pa; range of temperature: RT – 200 °C; β (φ (SiC) = 4.0 eV) = 4370.				

CFE under light conditions				
1D field emitters	Notes	Threshold field, E_{Th} [V / µm]	Turn-on field, <i>E_{TO}</i> [V / µm]	References
CuO nanobelts	Pressure of $5 \cdot 10^{-7}$ Pa; halogen lamp	-	-	Chen et al. ^{S23}
ZnO NWs	Pressure of 5·10 ⁻⁶ Torr; UV lamp at 362 nm	-	5.1(dark) / 2.1 (light) at a current density of 1 μA/cm ²	Chen et al. ⁵⁵
CuO NWs	Pressure of 4·10 ⁻⁶ Torr; UV lamp at 365 nm	-	8.3 (dark) / 7.5 (light) at a current density of 10 μA/cm ²	Juan et al. ⁵³
TiO ₂ nanostructures	Pressure of about 10 ⁻⁵ Pa; UV lamp at 365 and 405 nm	-	-	Wakaya et al. ^{S24}
β-Ga ₂ O ₃ NWs	Pressure of 5·10 ⁻⁶ Torr; UV lamp emitting at 254 nm	-	2 (dark) / 1.2 (light) at a current density of 10 μA/cm ²	Wu et al. ⁵⁴
undoped and In- doped ZnO nanorods	Pressure < 5·10 ⁻⁶ Torr; He-Cd laser (325 nm)	-	5.4 (undoped; dark), 0.8 (doped; dark) / 3.8 (undoped, light), 0.24 (doped, light)	Chang et al. ⁵⁶
Ga-doped ZnO nanorods	Pressure $< 5 \cdot 10^{-6}$ Torr; He-Cd laser (325 nm)	-	3.63 (dark), 3.15 (light)	Hsiao et al. ^{S25}
Undoped and Ga-doped ZnO nanorods	Pressure < 5·10 ⁻⁶ Torr; UV 325-nm light	-	5.4 (undoped, dark), 3.6 (doped, dark) / 3.8 (undoped, light), 3.1 (doped, light)	Chang et al. ⁵⁷
Mg-doped ZnO nanorods	Pressure < 5·10 ⁻⁶ Torr; UV 365-nm light	-	2.27 (dark) / 1.97 (light)	Liu et al. ⁵⁸
Bare and Ag- decorated ZnO nanorods	Pressure < 5·10 ⁻⁶ Torr; UV 365-nm light	-	6.7 (bare, dark), 3.93 (Ag-decorated, dark) / 3.87 (bare, light), 2.04 (doped, light)	Yang et al. ⁵⁹

Table S2 Review of CFE of semiconductor NWs under photon excitation

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