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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.

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	
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	The essure of about $5 \cdot 10^{-3}$	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	ressure 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 pr	essure of about 1.10^{-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 pressure 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	at pressure of $3 \cdot 10^{-5}$ Pa	a.		
Ga-catalyzed VLS-grown bamboo-like β-SiC NWs; highly faceted hexagonal cross-sections and sharp corners.	-	10	Shen et al. ³⁸	
FE meausrements at pressure of about $5 \cdot 10^{-7}$ Torr.				
Hierarchical single-crystalline β-SiC nanoarchitectures.	-	12	Shen et al. ³⁹	
FE meausrements at pressure of about $1.1 \cdot 10^{-5}$ Torr; report of two linear regimes.				

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
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	ents at pressure of about 5.1	10 ⁻⁵ Pa.	
MOCVD-grown β-SiC NWs.	$\begin{array}{c} 2 \ (\text{for I}_{Th}{=}5 \ \text{nA},\\ \text{corresponding to a}\\ \text{current density of } 0.025\\ \mu\text{A/cm}^2; \end{array}$	-	Kim et al. ⁴¹
FE meausrements at pressu	the of about 10^{-7} Torr; $\beta(\phi(S))$	SiC) = 5 eV) = 2000.	
Microwave assisted vapor-solid-grown ultrathin 3C–SiC nanobelts.	-	3.2	Wei et al. ⁴²
FE meausrem	ents at pressure of about 4.1	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 $d= 300, 400 and 500 \mum$	Yang et al. ⁴³
FE meausrements at pressure of about $2 \cdot 10^{-4}$ Pa; $\beta(\varphi(SiC) = 4.53 \text{ eV}) = 5241$.			
Catalyst-free tubular β -SiC nanostructures.	10 at a current density of 10 mA/cm^2	< 5	Cui et al. ⁴⁴
The pressure at which 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 meausrements 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. ^{S3}
FE meausrements at p	pressure of about $7 \cdot 10^{-5}$ Pa;	φ(SiC) = 5 eV.	

1D field emitters	Threshold field, E_{Th} [V / µm]	Turn-on field, <i>E_{TO}</i> [V / μm]	References		
Al2O3 decorated and bare tubular β-SiC (bunch-like) nanostructures.	23.5 (bare β -SiC nanostructures) / 5.37 (Al2O3 decorated β -SiC nanostructures) at a current density of 10 mA/cm ²	8.8 (bare β-SiC nanostructures) / 2.4 (Al2O3 decorated β- SiC nanostructures)	Cui et al. ⁴⁴		
The pressure at whi	ich FE were performed was r	not reported.			
Lawn-like 3C-SiC NWs; hexagonal cross section; presence of microtwins and SFs.	-	2.1	Chen et al. ⁴		
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. ^{S.}		
FE meausrements at pressure of	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.		
FE meausrem	ents at pressure of about 10 ⁷	⁷ Torr.			
CVD-grown nonaligned-SiC NWs on Si nanoporous pillar array; presence of SFs.	-	2.9	Wang et al.		
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}		
Fe-assisted VLS-grown β-SiC NWs on flexible carbon fabric; hexagonal cross section; presence of microtwins and SFs.	-	1.2	Wu et al.		

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 pressur	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	e of about $5 \cdot 10^{-5}$ Pa; β (φ (S	iC) = 4.0 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.	$6.7 (10 \text{ minutes of H}_2$ -	$3.2(10 \text{ minutes of H}_2$ -	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	
	treatment); at a current	minutes of N ₂ -	
	density of 10 mA/cm ²	treatment)	
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FE meausrements at pressure of about 10⁻⁷ Torr.

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	
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. ^{S14}	
FE meausrements at pressure	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. ^{\$15}	
FE meausrements at pre	essure of about $1.5 \cdot 10^{-7}$ Pa;	$\rho(SiC) = 4.0 \text{ eV}.$		
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	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	FE meausrements at pressure of about $1.5 \cdot 10^{-7}$ Pa; $\varphi(\text{SiC}) = 4.0 \text{ eV}$: $\beta(2.9 \cdot 10^7 \text{ NWs} / \text{cm}^2) = 3300$, $\beta(4.0 \cdot 10^7 \text{ NWs} / \text{cm}^2) = 3340$, $\beta(5.7 \cdot 10^7 \text{ NWs} / \text{cm}^2) = 3217$.			
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 2.0·10 ⁻⁷ Pa; range of temperature: RT – 500 °C; β (ϕ (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}	
FE meausrements at pressure of about $3.0 \cdot 10^{-7}$ Pa; range of temperature: RT – 500 °C; β (ϕ (SiC) = 4.0 eV) = 2671.				

CFE from SiC nanostructures under dark conditions			
1D field emitters	Threshold field, <i>E_{Th}</i> [V / μm]	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; $\varphi(SiC) = 4.0$ eV: β (bare NWs) = 1150, β (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; $\beta(\phi(SiC) = 4.0 \text{ eV}) = 4370$.			

CFE under light conditions				
1D field emitters	Notes	Threshold field, E_{Th} [V / μ m]	Turn-on field, E_{TO} [V / μ m]	References
CuO nanobelts	Pressure of 5.10 ⁻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 μ A/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 < 5·10 ⁻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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