

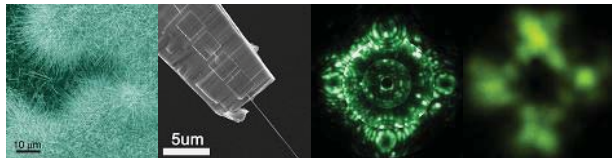


HfCナノワイヤーの合成と電界放出特性に関する研究

Synthesis, Characterization and Field Emission Properties of Hafnium Carbide Nanowires

独立行政法人 物質・材料研究機構

一次元ナノ材料グループ 元 金石 (Yuan Jinshi)



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Self-Introduction

| | | |
|--------------------------------|---|---------------------|
| 2002.09-2006.06 | Tsinghua University, China. Department of Mechanical Engineering. | Bachelor |
| 2006.09-2009.06 | Tsinghua University, China. Department of Mechanical Engineering. Major of Materials Processing Engineering. Functional Thin Film Lab. | Master |
| 2009.08-2012.07 | University of Tsukuba, Japan. Graduate School of Pure and Applied Sciences. Major of Materials Science and Engineering. | Doctor |
| 2012.07-present | National Institute for Materials Science. One-Dimensional Nanomaterials Group. | Post-doc Researcher |
| Low-Dimensional Nanomaterials. | Research Interests: Synthesis, Characterization and Applications of Low-Dimensional Nanomaterials. | 46 |



Publication List

* 1) Peer Reviewed Papers

- * 1. **J. S. Yuan**, H. Zhang, J. Tang, N. Shinya, K. Nakajima, and L.-C. Qin, "Field emission from single-crystalline HfC nanowires", *Appl. Phys. Lett.* 2012, 100: 113111.
 - * 2. **J. S. Yuan**, H. Zhang, J. Tang, N. Shinya, K. Nakajima, and L.-C. Qin, "Synthesis and characterization of single crystalline hafnium carbide nanowires", *J. Am. Ceram. Soc.*, DOI: 10.1111/j.1551-2916.2012.05247.x.
 - * 3. **J. S. Yuan**, H. Zhang, J. Tang, N. Shinya, Y. X. Lin, and L.-C. Qin, "Synthesis and characterization of single crystalline GdB₄Si₂ nanostructures", *J. Mater. Sci.*, DOI : 10.1007/s10853-012-6911-3.
 - * 4. H. Zhang, J. Tang, **J. S. Yuan**, J. Ma, N. Shinya, K. Nakajima, H. Muekami, T. Ohkubo, and L.-C. Qin, "Nanostructured LaB₆ field emitter with lowest apical work function", *Nano Lett.*, 10 (2010) 3539–3544.
- ### * 2) Oral Presentations
- * 1. **J. S. Yuan**, H. Zhang, J. Ma, N. Shinya, L.-C. Qin, J. Tang, "Preparation and characterization of LaB₆ nanowires with dean surfaces", the 19th Academic Symposium of MRS-Japan 2009, December 7-9 2009, Yokohama.
 - * 2. **J. S. Yuan**, H. Zhang, J. Tang, N. Shinya, K. Nakajima, and L.-C. Qin, "Single HfC nanowire point electron source", 2010 MRS Fall Meeting, November 29-December 3, Boston, MA, US.
 - * 3. **J. Yuan**, H. Zhang, J. Tang, N. Shinya, K. Nakajima, and L.-C. Qin "Hafnium carbide nanowire-based field emitter of electrons"

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Outline

1. Background
 - * One-dimensional nanomaterials and their applications.
 - * Transition metal carbide nanowires as field emission point source.
2. Progress
 - * Synthesis and characterization of HfC nanowire.
 - * Field emission performance of HfC nanowire-based field emitter.
3. Summary

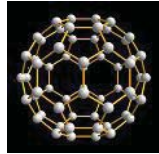
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Nanostructured Materials



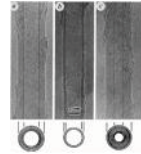
"There's Plenty of Room at the Bottom." — Richard Feynman.

Fullerene Structure



Discovered by Robert Curl, Harold Kroto and Richard Smalley in 1985

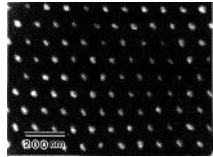
Carbon Nanotube



Iijima, S. (1991). Nature, 354, 56

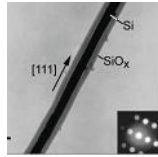


0D-Nanodot



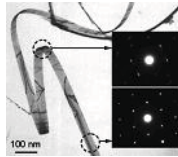
Masuda, H. (1996). Jpn. J. Appl. Phys., 35, 126

1D-Nanowire



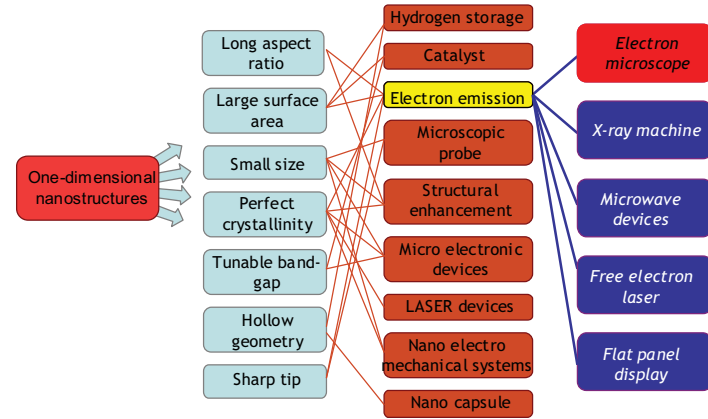
Morales, A.M., Lieber, C.M. (1998). Science, 279, 208

2D-Nanobelt

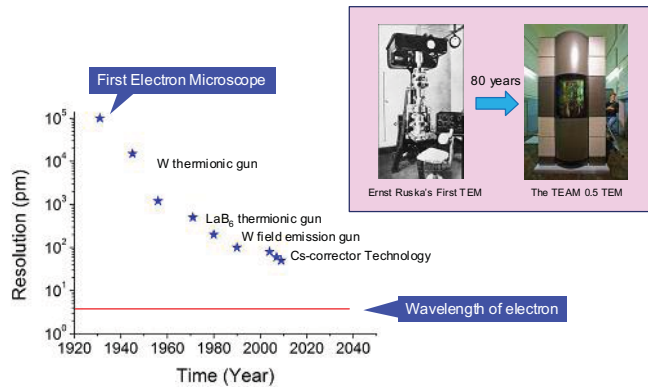


Kong, X.Y., Wang, Z.L. (2008). Nano Letter, 12, 1625

One-Dimensional Nanostructures

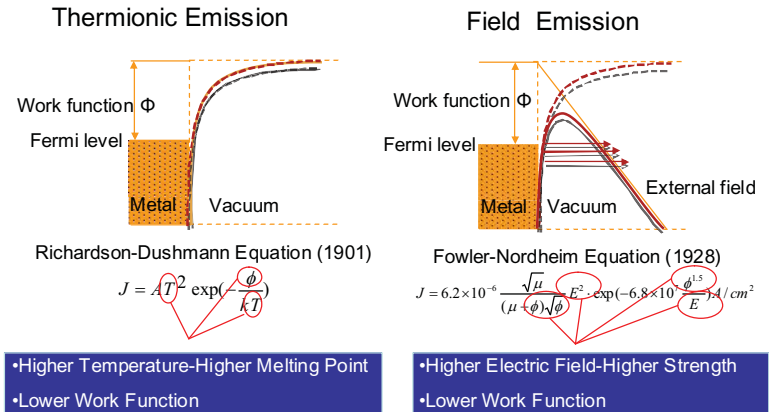


Development of Transmission Electron Microscope



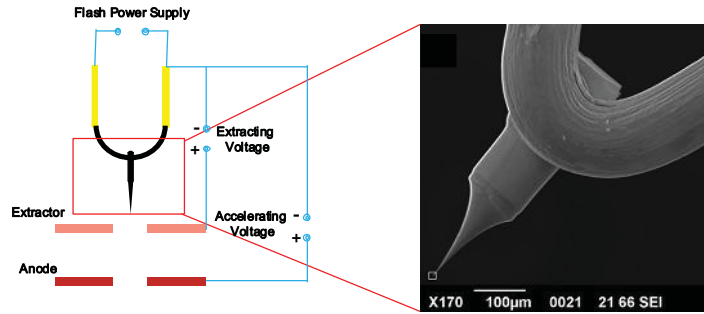
Milestones in the development of electron microscope

Electron Emission



Materials with low work function and high strength are needed.

Field Emission Gun



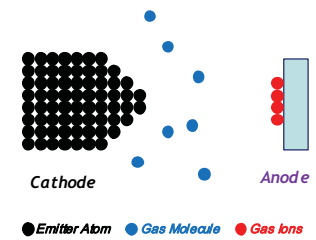
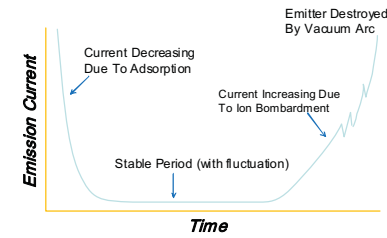
Simplified schematic of a field emission gun

Houdellier F. et al, (2012), 50, 2037

For high electric field, a very sharp tip is needed. The field factor $\beta = E/V$ can be estimated as $1/5r$ to $1/100r$, where r is the radius of curvature of the tip.

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Field Emission Stability



$$\frac{I(t)}{I_0} = \left(1 - \frac{n_c S(\theta)}{N_i \beta_i}\right) + \frac{n_c S(\theta)}{N_i \beta_i} \exp\left(-\frac{t N_i \beta_i}{n_0}\right)$$

Initial Decay

$$\frac{\Delta I}{I} = f(N_i) + c$$

Bombarding Ions per Unit Time at the Emitter Surface

$$N_i = 3.1 \times 10^{18} \beta_i \left(\frac{n_c r_0}{R}\right)^2 I + 1.7 \times 10^{13} \sigma_c (r_i - r_0) IP$$

The function S and f are all related to the emitter materials' properties to resist contamination and destruction.

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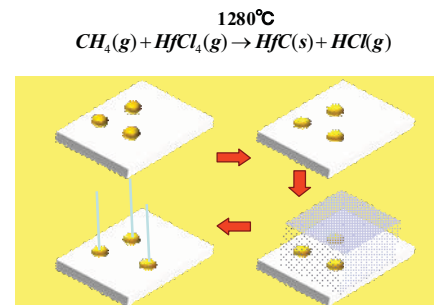
Material Candidates



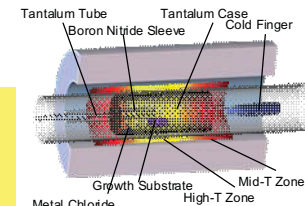
| Material | ϕ (eV) | T_m (°C) | Resistivity (Ωcm) | Hardness (Kg/mm ²) |
|------------------|-------------|------------|----------------------|--------------------------------|
| LaB ₆ | 2.6 | 2535 | 1.5X10 ⁻⁵ | 2470 |
| GdB ₆ | 1.55-3.44 | 2100 | 1.3X10 ⁻⁵ | 2091 |
| HfC | 3.4 | 3890 | 4.5X10 ⁻⁵ | 2860 |
| TiC | 3.3 | 3160 | 5.3X10 ⁻⁵ | 2930 |
| TaC | 3.6 | 3880 | 4.1X10 ⁻⁵ | 1570 |
| Graphite C | 4.3 | 3652 | 1X10 ⁻³ | |
| W | 4.54 | 3410 | 5.5X10 ⁻⁶ | 300 |
| SrO | 1.43 | 2430 | 18 | |

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Synthesis of HfC Nanowire



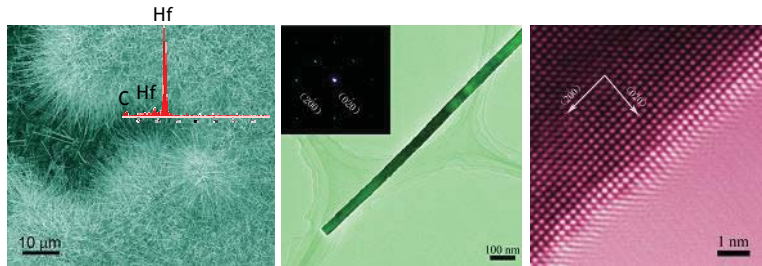
HfC Nanowire Synthesis Schematics



High Vacuum Metal Boride/Carbide Nanowire Synthesis System

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Morphology , Composition and Structure

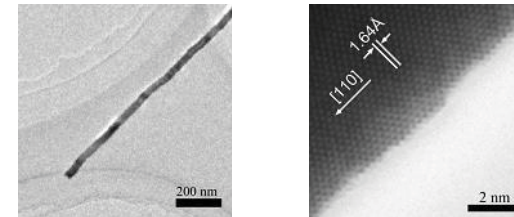


SEM image: HfC Growth Substrate

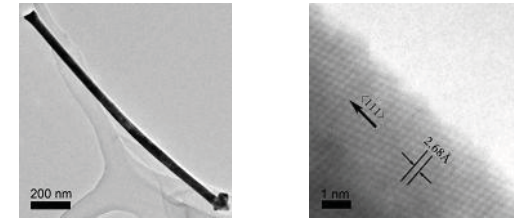
TEM image: Individual HfC Nanowire

Uniform, Clean Single Crystalline Nanowires Along <100> Direction.
This is the *first successful synthesis* on HfC nanowires.

Nanowires Along Other Directions

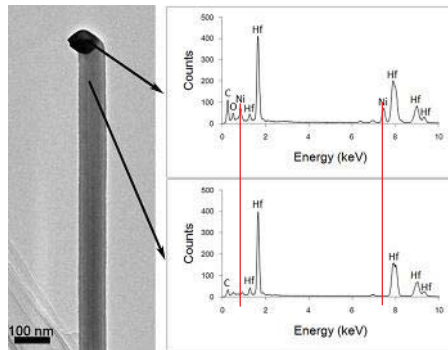


<110> oriented nanowire



<111> oriented nanowire

Composition Distribution



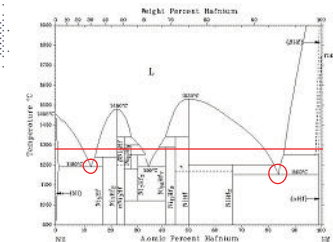
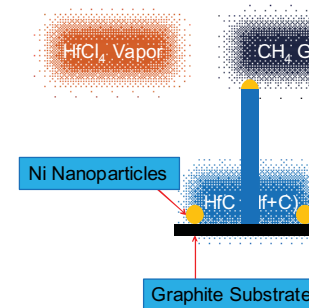
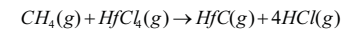
EDS results from a nanowire

The Ni was only detected in the particle at the tip of the nanowire.

This result indicated the growth of HfC nanowire followed the vapor-liquid-solid (VLS) mechanism.

Growth Mechanism

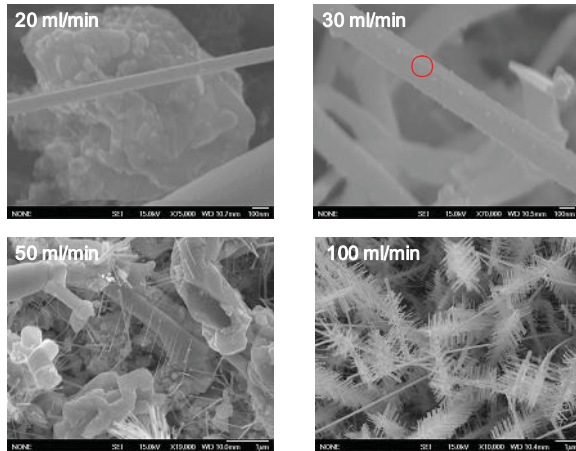
Vapor – Liquid – Solid (VLS) Mechanism



Different Morphologies

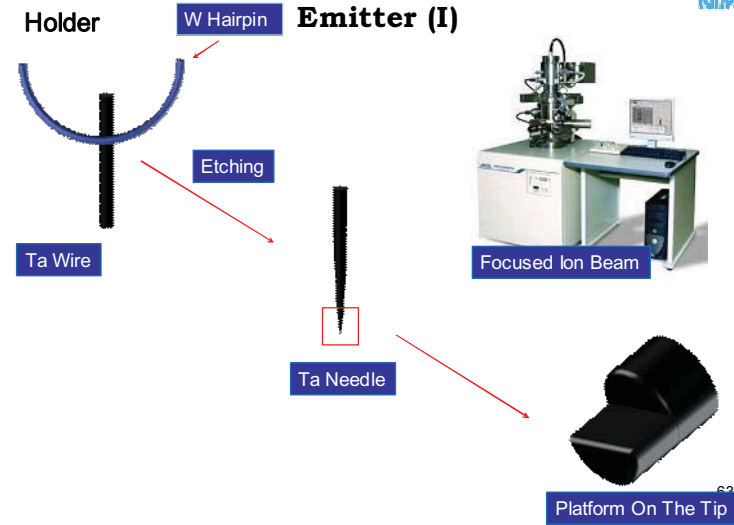


Under different flow rate of CH₄:



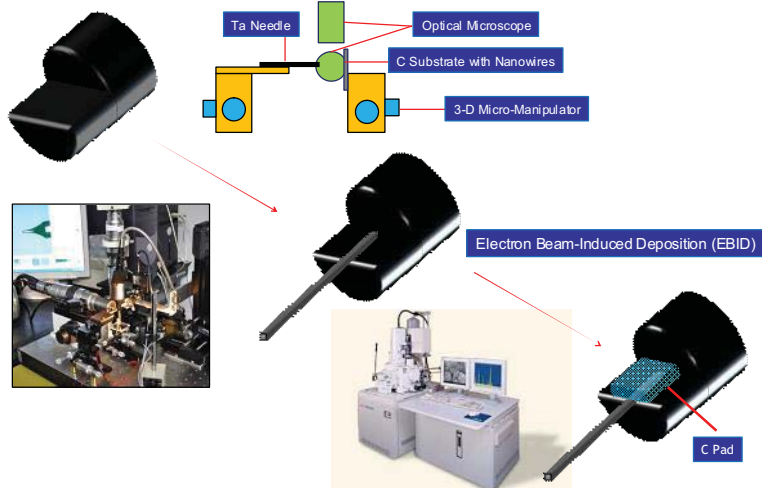
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Fabrication of Nanowire-Based Field Emitter (I)



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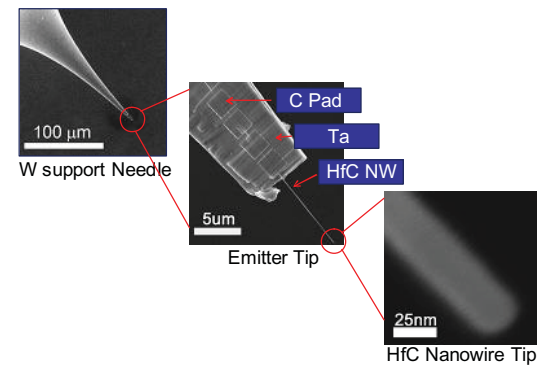
Fabrication of Nanowire-Based Field Emitter (II)



Fabrication of Nanowire-Based Field Emitter (III)

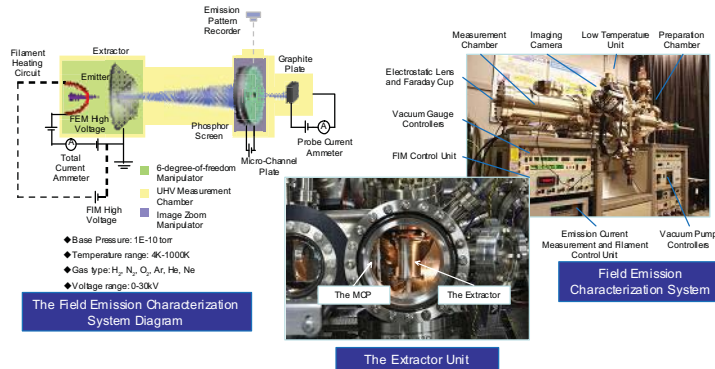


SEM Images



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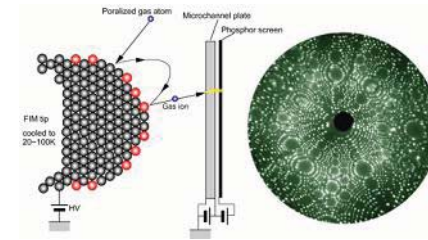
Field Emission Characterization System



The Extractor Unit

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Field Ion Microscope (FIM) and Field Evaporation



Schematic of field ion microscope

<http://www.nims.go.jp/apfm/fim.html>

When the electric field is high enough, the atoms on the surface are pulled out.

Threshold electric field for field evaporation:

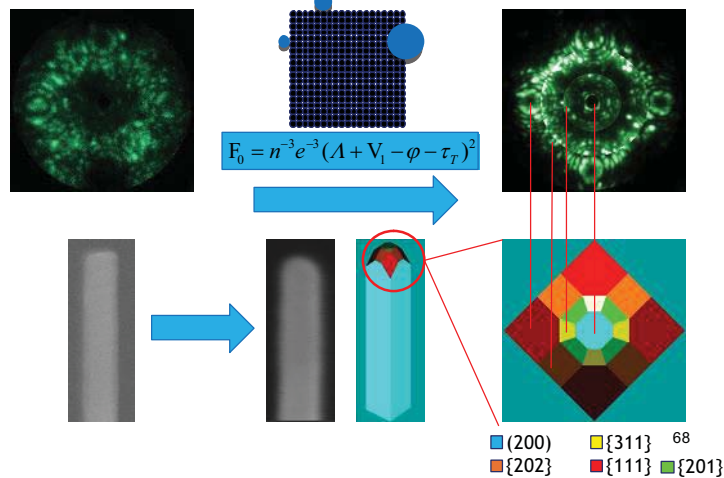
$$F_0 = n^{-3} e^{-3} (A + V_1 - \phi - \tau_T)^2$$

Local brightness:

$$I \propto F_L \propto \frac{1}{R_c}$$

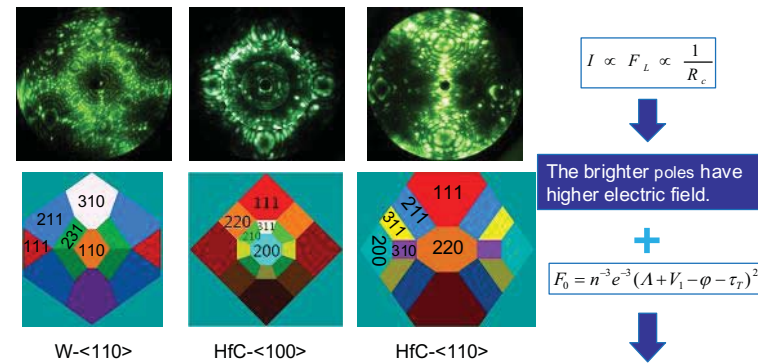
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Field Ion Microscope (FIM) and Field Evaporation



■ {200} ■ {311} ⁶⁸
■ {202} ■ {111} ■ {201}

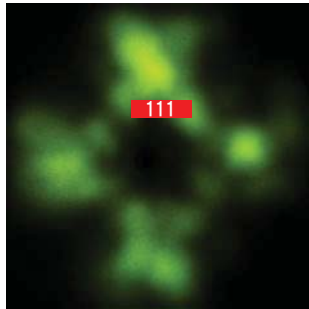
FIM and Work Function



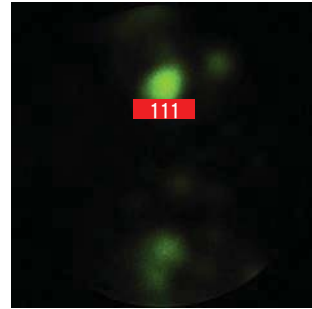
Work Function Sequence: W: $\phi_{\{111\}} < \phi_{\{310\}} < \phi_{\{110\}}$

HfC: $\phi_{\{111\}} < \phi_{\{220\}} \leq \phi_{\{200, 210, 311, \dots\}}$ ⁶⁹

Field Emission Pattern



HfC-⟨100⟩ - 4 fold

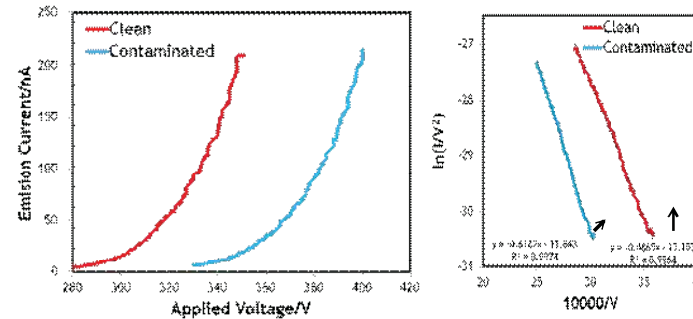


HfC-⟨110⟩ - 2 fold

Only {111} areas are bright which means the {111} crystal planes have the lowest work function.

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I-V Curve



$$J = 1.54 \times 10^{-6} \frac{F^2}{\phi} \exp\left(-6.3 \times 10^9 \frac{\phi^2}{F}\right) \Rightarrow \ln\left(\frac{I}{V^2}\right) = \ln\left(A \cdot 1.54 \times 10^{-6} \frac{\beta^2}{\phi}\right) - 6.83 \times 10^7 \frac{\phi^2}{\beta} \frac{1}{V}$$

Good Linearity in F-N plot

Cold Emission

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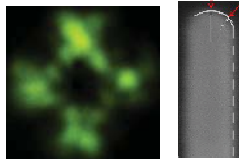
Calculation of Work Function



$$J = 1.14 \times 10^9 \phi^2 e^{10.4/\phi^{1/2}} \frac{e^{-2.3m/V}}{(m/V)^2} \text{ where } m = -\frac{d[\log_{10}(I/V^2)]}{d(1/V)} = -\frac{1}{\ln 10} \frac{d[\ln(I/V^2)]}{d(1/V)} = -\frac{1}{\ln 10} k_1$$

Emitting Area:

Clean Surface



R=23.6nm
r=11.7nm

Dirty Surface

The emitted electrons are expected to come out from the whole surface.

$$A = 2.24 \times 10^{-12} \text{ cm}^2$$

$$J = I/A = I/2.24 \times 10^{-12} \text{ Acm}^{-2}$$

$$A = 14.90 \times 10^{-12} \text{ cm}^2$$

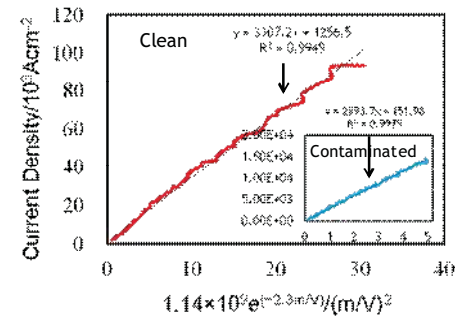
$$J = I/A = I/14.90 \times 10^{-12} \text{ Acm}^{-2}$$

Calculation of Work Function



$$J = 1.14 \times 10^9 \phi^2 e^{10.4/\phi^{1/2}} \frac{e^{-2.3m/V}}{(m/V)^2}$$

$$k_2 = \phi^2 e^{10.4/\phi^{1/2}}$$



$$k_2^{\text{clean}} = 3307.2$$

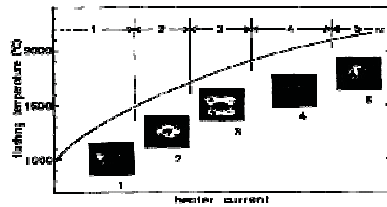
$$k_2^{\text{dirty}} = 2893.7$$

$$\phi_{\text{clean}} = 3.4 \text{ eV}$$

$$\phi_{\text{dirty}} = 4.0 \text{ eV}$$

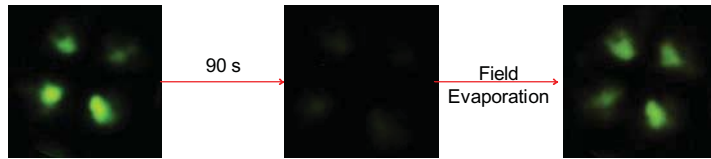
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Emission Stability



H. Adachi, C. Oshima, etc., Appl. Phys. Lett. 43(1983), 702

Emission pattern changed with different flash process conditions :
1. Composition deviation; 2. Devastated surface state.



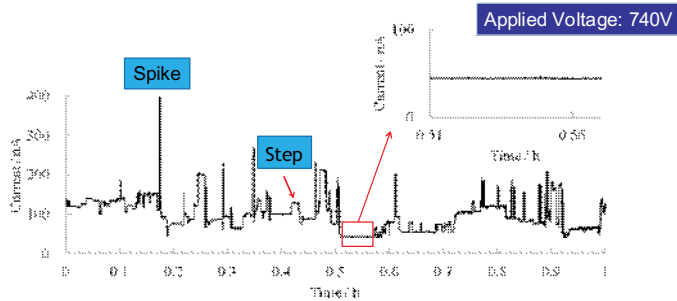
Repeatable Emission Pattern

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Emission Stability



Emission Current from an As-Grown Nanowire



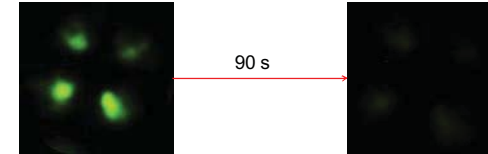
1. The noise is step and spike noise similar to C materials which are inert to gas adsorption.
2. The step and spike type noises are caused by ions of ambient gas molecules in vacuum ionized by the field emission current.

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Emission Stability

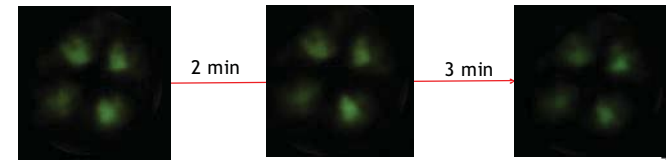


At room temperature



The brightness decayed by more than 90%, which was caused by the adsorption of the molecules in the chamber.

At liquid N₂ temperature



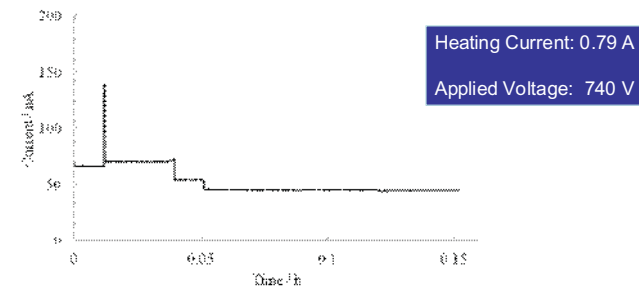
We can expect good stability in a high vacuum condition.

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Emission Stability



Thermal - Assisted Emission Current from an As-Grown Nanowire

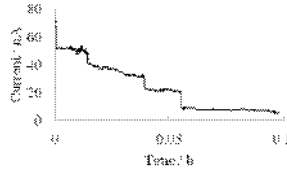


1. By heating the tip surface we would expect fewer adsorbed molecules on the surface than at room temperature.
2. Heating the tip can remove the dangling bonds of the adsorbed H₂ molecules.

Emission Stability



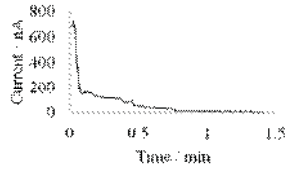
Emission Current from a Flashed As-Grown Nanowire



Flashing Current: 0.88 A

Applied Voltage: 600 V

1. A fast decay occurred that means the terminated layer of the nanowire became into Hf atoms.
2. There are still some steps which means the C layer was not removed completely.



Flashing Current: 1.21 A

Applied Voltage: 600 V

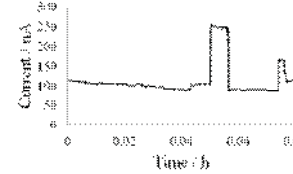
After flashed under higher current, the decay was faster and the steps disappeared. The outmost atoms of the tip were totally Hf.

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Emission Stability



Emission Current from an O₂-Treated Nanowire



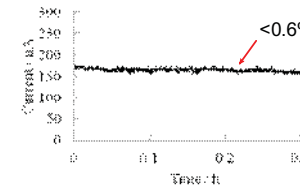
Treating Current: 0.79 A

O₂ Pressure: 1.1×10⁻⁸ Torr

Applied Voltage: 900 V

Little decay and fluctuation with only some steps.

Thermal – Assisted Emission Current from an O₂-Treated Nanowire



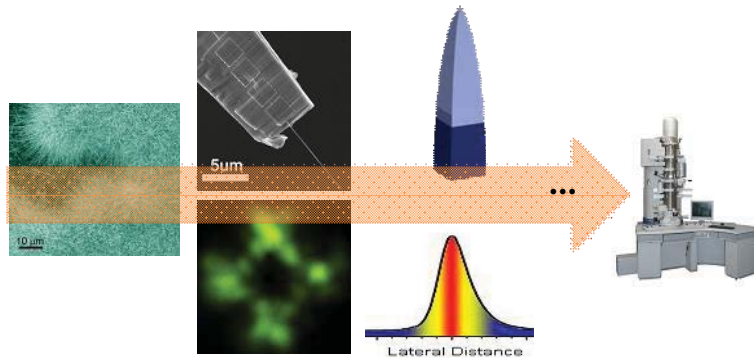
Heating Current: 0.79 A

Applied Voltage: 700 V

Stable emission current with fluctuation noise less than 0.6%.

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Summary



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Acknowledgement



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Prof. Tang
Japan

Prof. Qin
USA

Dr. Zhang
Japan

Prof. Shinya
Japan



Group members

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- Nanotechnology Network Project of the Ministry of Education, Culture, Sports, and Technology (MEXT)

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