電子源の仕事関数

その他（別言語等）のタイトル	Possibility of the Schottky emitter with low work function surface
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電子源の仕事関数

Possibility of the Schottky emitter with low work function surface

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2018/3/1 第16回真空ナノエレクトロニクスシンポジウム

Background (1)

電界放射電流密度と陰極表面の仕事関数との関係

○Fowler-Nordheim Ex.

$$\frac{I}{S} = 1.54\times10^{-6}\times\frac{F^2}{\phi\, t^2_{(y)}}\exp\left(-6.83\times10^{7}\frac{\upsilon_{(y)}\phi^{3/2}}{F}\right) \qquad [\mathrm{A/cm^2}]$$

$$F = \beta\times V \quad [\mathrm{V/cm}] \qquad \beta = \frac{1}{5\times r} \quad [1/\mathrm{cm}]$$

Cathode tip

I : emission current [A] S : emission area [cm^2] F : field strength [V/cm]
ϕ : work function [eV] β: cathode structure constant[1/cm] V : voltage [V]
r : tip radius [cm]

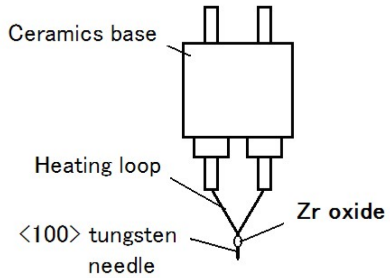
熱電子電流密度と陰極表面の仕事関数との関係

○Richardson Ex.

$$\frac{I}{S} = AT^2\exp(-\phi/kT) \qquad [\mathrm{A/cm^2}]$$

Background (2)

ZrO/W(100) Schottky emitter



- Work function of W(100) bare surface is 4.6 eV.
- But it can be reduced to 2.7 eV by heating it in oxygen ambient with slight layer of Zr.
- The lower the value of the work function is, the more electrons are emitted from the emitter.

Our goal was to make lower work function emitter than ZrO/W(100).

Purpose

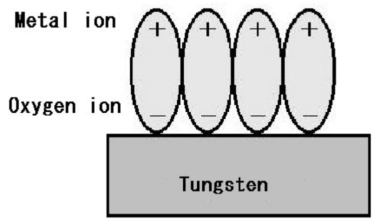
We have tried
to study the reducing work function mechanism and
to search materials better than Zr oxide.

In this research,
We measured the work function of W(100) modified by **group III, IV metal oxide** by using

1. **FEM (field emission microscope)**
2. **Retarding method**
3. **PEEM (photoemission electron microscope)**

1. Selection of materials for emitter modification (1)

1.1 Mechanism of reducing work function



- Electric dipoles on a metal surface are believed to reduce the work function remarkably.
- The dipole moment has a tight relation to the **P value** which is defined as followings:

P=(Eo-Ex)(Ro+Rx)
Eo: Electro-negativity for oxygen
Ex: Electro-negativity for the metal
Ro: Ionic radius for oxygen
Rx: Ionic radius for the metal

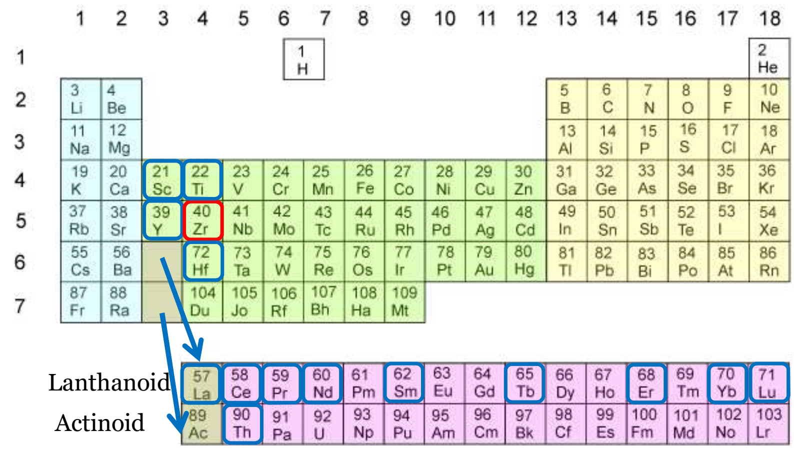
1. Selection of materials for emitter modification (3)

Table 1 P value

	Pair		Electro-negativity (Pauling)	Ionic radius (nm)	P value	
Group III	Sc	-O	1.36	0.075	0.442	
	Y	-O	1.22	0.090	0.511	
	La	-O	1.10	0.103	0.564	Lanthanoid
	Ce	-O	1.12	0.087	0.517	
	Pr	-O	1.13	0.099	0.547	
	Nd	-O	1.14	0.098	0.543	
	Sm	-O	1.17	0.096	0.531	
	Tb	-O	1.10	0.092	0.539	
	Er	-O	1.24	0.089	0.499	
	Yb	-O	1.10	0.087	0.495	
	Lu	-O	1.27	0.086	0.486	
	Th	-O	1.30	0.094	0.492	Actinoid
Group IV	Ti	-O	1.54	0.086	0.429	
	Zr	-O	1.33	0.072	0.439	
	Hf	-O	1.30	0.071	0.447	

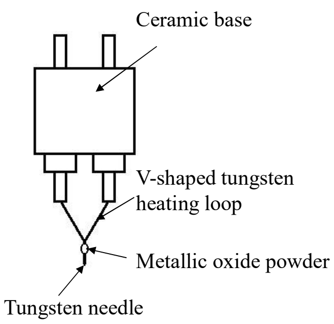
1. Selection of materials for emitter modification (2)

1.2 Periodic table and selected materials



2. Method of work function measurement (1)

2.1 FEM (1)



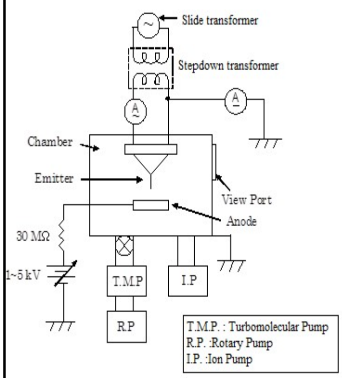
The emitter sample

○ The emitter fabrication

1. <100> or <110> directed tungsten wire is spot welded to vertex of a heating loop.
2. The sample is electro-chemically cleaned.
3. The sample is electro-chemically sharpened.
4. Small quantity of metallic oxide powder is put on the shaft.

2. Method of work function measurement (2)

2.1 FEM (2)



Experimental setup

○FEM procedure

1. The sample was put on the ultrahigh vacuum chamber at 10^{-7} Pa.
2. The sample was heated at 1200 to 2700 K for several minutes.
3. When high voltage was applied between the sample emitter and the anode), the emission pattern from the sample was projected on the phosphor screen.
4. After low work function surface is formed, total emission current is measured.

2. Method of work function measurement (3)

2.1 FEM (3)

○Fowler-Nordheim Plot

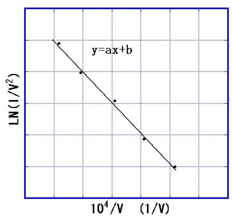
Cathode tip

$$\frac{I}{S} = 1.54\times10^{-6}\times\frac{F^2}{\phi\, t^2_{(y)}}\exp\left(-6.83\times10^{7}\,\frac{\upsilon_{(y)}\phi^{3/2}}{F}\right) \qquad [\mathrm{A/cm^2}]$$

$$F = \beta\times V \quad [\mathrm{V/cm}] \qquad \beta = \frac{1}{5\times r} \quad [1/\mathrm{cm}]$$

I : emission current [A]	S : emission area [cm^2]	F : field strength [V/cm]
φ: work function [eV]	β: cathode structure constant[1/cm]	V : voltage [V]
r : tip radius [cm]		

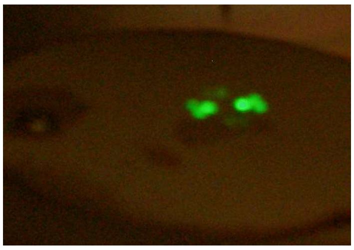
$$\ln\left(\frac{I}{V^2}\right) = \left\{\left(\frac{-6.83\times10^{7}\times\phi^{3/2}}{\beta}\right)\times\left(\frac{1}{V}\right)\right\} + \ln\left(1.54\times10^{-6}\,\frac{S\times\beta^2}{\phi}\right)$$



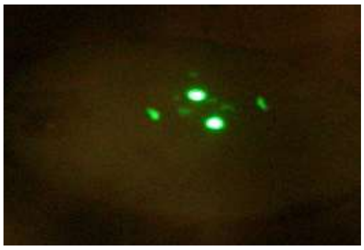
3. Experimental results (1)

3.1 FEM (1)

○Sc – oxide /W emitter



A field emission pattern from before treated Sc-oxide/W emitter.



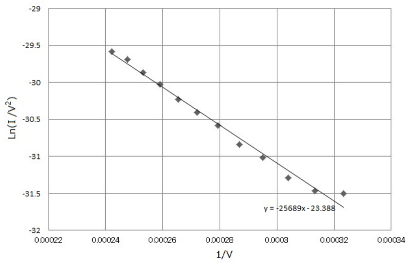
A field emission pattern from after treated Sc-oxide/W emitter.

- The emission pattern is changed to <u>a two-fold symmetry with two bright spots</u> after heating.
- The work function of Sc-oxide/W(100) sample was estimated by using <u>F-N plot</u>.

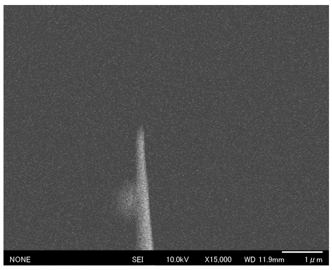
3. Experimental results (3)

3.1 FEM (3)

○Sc – oxide /W emitter



F-N Plot of Sc-oxide/W emitter
The slope = -25689



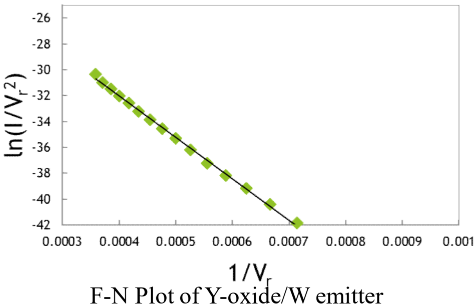
The radius of the Sc-oxide/W emitter
The radius r=0.167 μm

- The work function estimated from <u>the slope of F-N plot</u> and <u>the radius of the sample</u>.
- The work function was **<u>2.7 eV</u>**.

3. Experimental results (2)

3.1 FEM (2)

○Y – oxide /W emitter



F-N Plot of Y-oxide/W emitter
The slope = -3.2×10^4

The radius of the Sc-oxide/W emitter
The radius r=0.2 µm

- The work function estimated from the slope of F-N plot and the radius of the sample.
- The work function was **2.8 eV**.

3. Experimental results (4)

3.1 FEM (4)

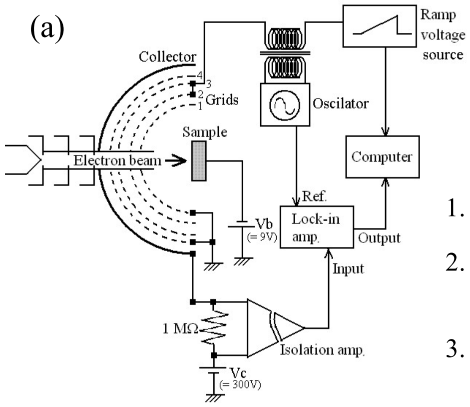
Table 2 Work function (FEM)

Group	Pair		Electro-negativity (Pauling)	Ionic radius (nm)	P value	Work function (eV) FEM	Retarding	PEEM	
Group III	Sc	-O	1.36	0.075	0.442	2.7			Lanthanoid
	Y	-O	1.22	0.090	0.511	2.0～3.1			
	La	-O	1.10	0.103	0.564	2.5, 2.9～3.3			
	Ce	-O	1.12	0.087	0.517	2.9～3.1			
	Pr	-O	1.13	0.099	0.547	2.5			
	Nd	-O	1.14	0.098	0.543	2.5			
	Sm	-O	1.17	0.096	0.531	3.4			
	Tb	-O	1.10	0.092	0.539	×			
	Er	-O	1.24	0.089	0.499	2.4			
	Yb	-O	1.10	0.087	0.495				
	Lu	-O	1.27	0.086	0.486	2.6			
	Th	-O	1.30	0.094	0.492	2.7			Actinoid
Group IV	Ti	-O	1.54	0.086	0.429	4.57			
	Zr	-O	1.33	0.072	0.439	2.7～2.9			
	Hf	-O	1.30	0.071	0.447				

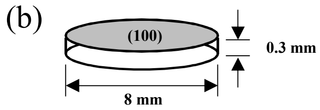
2. Method of work function measurement (4)

2.2 Retarding method (1)

(a)



(b)

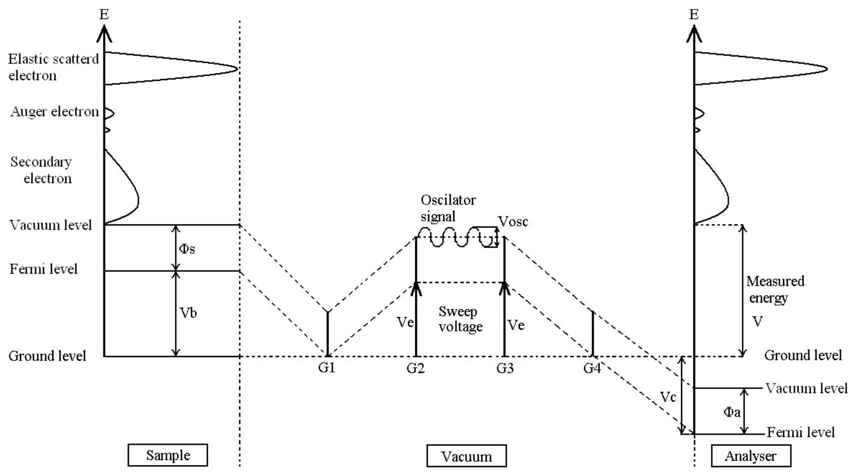


1. The first electron beam is hit the sample.
2. The electrons in the sample is exited and shot as secondary electrons.
3. The electron is collected at the collector and analyzed by the lock-in amplifier and PC.

(a) Experimental setup
(b) Experimental sample（W(100) single crystalline disk）

2. Method of work function measurement (5)

2.2 Retarding method (2)



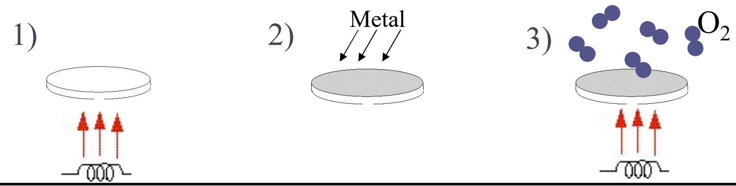
2. Method of work function measurement (6)

2.2 Retarding method (3)

1. To clean the surface of the W(100) single crystalline disk sample, the sample is heated at 2200 K for 30 seconds in an ultra high vacuum chamber at 10^{-7} Pa.

2. Metal was deposited at several monolayers onto the W(100) sample in an ultra high vacuum chamber at 10^{-7} Pa.

3. The sample was heated at 1100 K for 5 minutes in oxygen ambient at 10^{-5} Pa, resulting in producing metallic oxide on the W(100) sample.

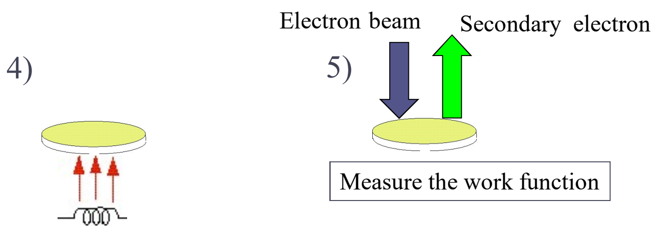


2. Method of work function measurement (7)

2.2 Retarding method (4)

4. After evacuating the oxygen, the sample is heated for 10 seconds in an ultrahigh vacuum at 10^{-7} Pa. The heating temperature is raised from 1100 K to 2200 K at an interval of 100 K.

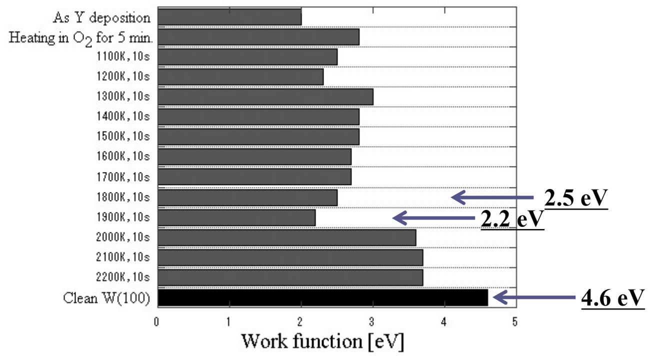
5. The work function of the sample is measured just after every flash heating.



3. Experimental results (4)

3.2 Retarding method (1)

○Y – oxide /W(100)



- The lowest work function of the sample is measured just after flash heating at 1900 K.

3. Experimental results (5)

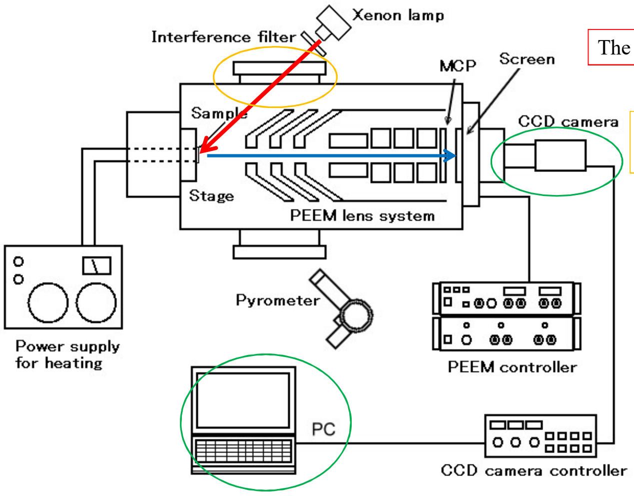
3.2 Retarding method (2)

Table 3 Work function (Retarding method)

	Pair		Electro-negativity (Pauling)	Ionic radius (nm)	P value	Work function (eV)			
						FEM	Retarding	PEEM	
Group III	Sc	-O	1.36	0.075	0.442	2.7			Lanthanoid
	Y	-O	1.22	0.090	0.511	2.0～3.1	2.2		
	La	-O	1.10	0.103	0.564	2.5, 2.9～3.3			
	Ce	-O	1.12	0.087	0.517	2.9～3.1			
	Pr	-O	1.13	0.099	0.547	2.5	2.7, 3.6		
	Nd	-O	1.14	0.098	0.543	2.5			
	Sm	-O	1.17	0.096	0.531	3.4			
	Tb	-O	1.10	0.092	0.539	×			
	Er	-O	1.24	0.089	0.499	2.4			
	Yb	-O	1.10	0.087	0.495				
	Lu	-O	1.27	0.086	0.486	2.6			
	Th	-O	1.30	0.094	0.492	2.7			Actinoid
Group IV	Ti	-O	1.54	0.086	0.429	4.57			
	Zr	-O	1.33	0.072	0.439	2.7～2.9			
	Hf	-O	1.30	0.071	0.447				

2. Method of work function measurement (8)

2.3 PEEM (1)



The light is irradiated by the sample.

The wavelength of the light is selected by the interference filter.

The photoelectrons is amplified by MCP, and projected on the screen.

The image is captured by the CCD camera, and analyzed by the PC.

Experimental setup

2. Method of work function measurement (9)

2.3 PEEM (2)

1. Metallic oxide powder was put on the W(100) single crystal surface, after the sample was introduced in an ultrahigh vacuum chamber at 10^{-7} Pa.

2. The sample was flash heated at 2100 K, afterward the sample was irradiated by a selected wave length light with the interference filter. The photoemission pattern was obtained by PEEM system.

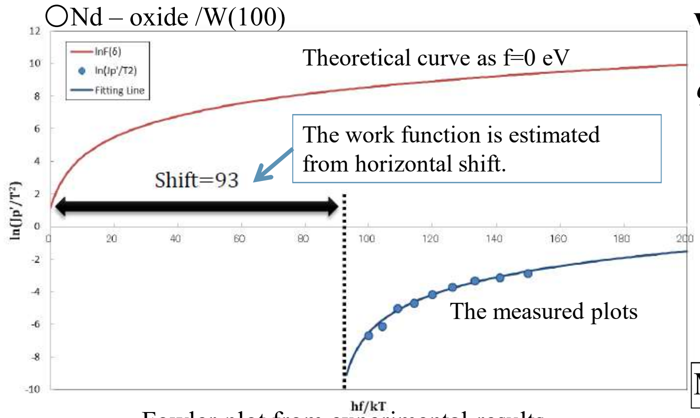
3. The work function of the sample was estimated by using with Fowler plot that was produced from the brightness of the photoemission pattern.

It is possible to estimate the intrinsic work function, because the work function is essentially defined by photoelectric effect.

3. Experimental results (6)

3.3 PEEM (1)

○Nd – oxide /W(100)



Fowler plot from experimental results.

Work function

$$\phi = \frac{shift \times kT}{e}$$

$= \mathbf{2.5\ eV}$

Material constant

f: frequency of wavelength	h: Planck's constant
T: sample temperature (absolute value)	k: Boltzmann's constant
Jp: emission current	e: elementary electron charge

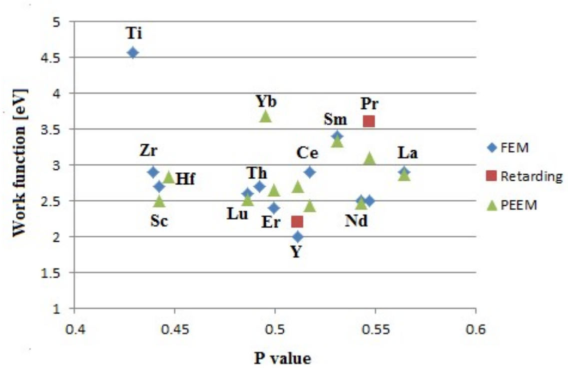
3. Experimental results (7)

3.3 PEEM (2)

Table 4 Work function (PEEM)

	Pair		Electro-negativity (Pauling)	Ionic radius (nm)	P value	Work function (eV) FEM	Retarding	PEEM	
Group III	Sc	-O	1.36	0.075	0.442	2.7		2.5	
	Y	-O	1.22	0.090	0.511	2.0～3.1	2.2	2.7～2.8	
	La	-O	1.10	0.103	0.564	2.5, 2.9～3.3		2.87～2.90	Lanthanoid
	Ce	-O	1.12	0.087	0.517	2.9～3.1		2.44～2.50	Lanthanoid
	Pr	-O	1.13	0.099	0.547	2.5	2.7, 3.6	3.11～3.14	Lanthanoid
	Nd	-O	1.14	0.098	0.543	2.5		2.47	Lanthanoid
	Sm	-O	1.17	0.096	0.531	3.4		3.34	Lanthanoid
	Tb	-O	1.10	0.092	0.539	×			Lanthanoid
	Er	-O	1.24	0.089	0.499	2.4		2.65	Lanthanoid
	Yb	-O	1.10	0.087	0.495			3.68	Lanthanoid
	Lu	-O	1.27	0.086	0.486	2.6		2.52～2.56	Lanthanoid
	Th	-O	1.30	0.094	0.492	2.7			Actinoid
Group IV	Ti	-O	1.54	0.086	0.429	4.57			
	Zr	-O	1.33	0.072	0.439	2.7～2.9			
	Hf	-O	1.30	0.071	0.447			2.84～2.90	

4. Summary



- The work function of the tungsten surface is successfully reduced modified by **<u>group III and IV metallic oxide</u>**.

3. Experimental results (9) 1999

Emission microscope for a field emitter array.

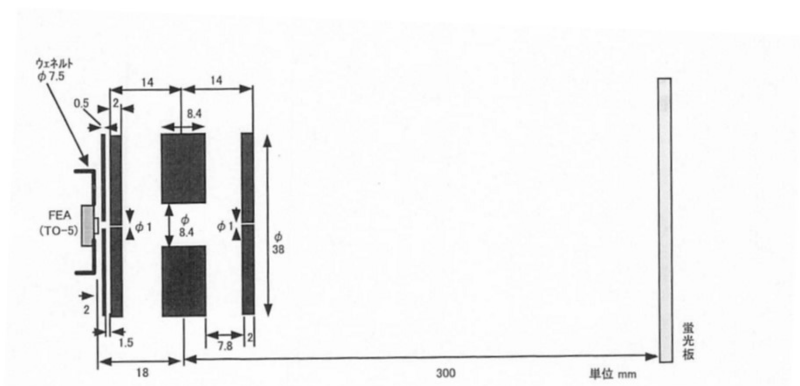


図2-9 レンズの配置図

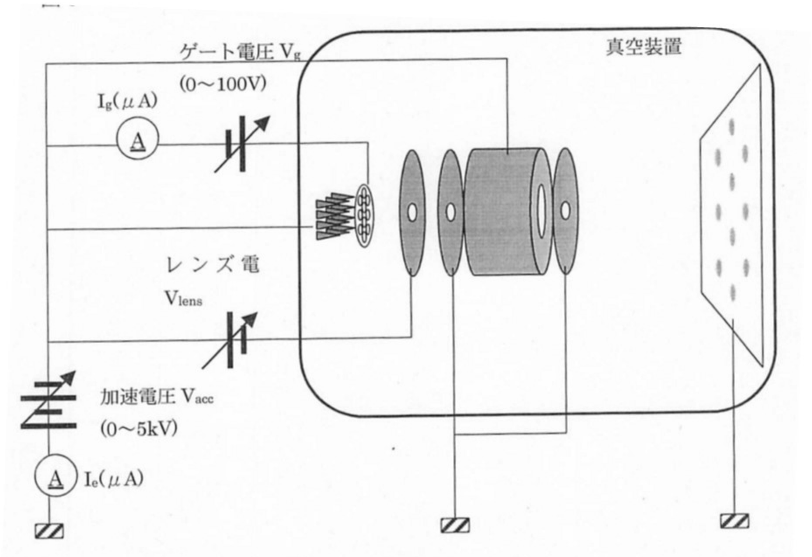


図３－４　放射顕微鏡の構成と電位配置

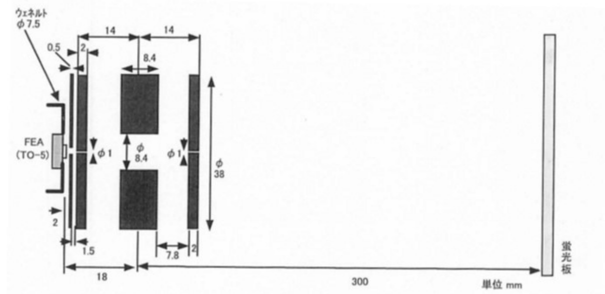


図２‐９　レンズの配置図

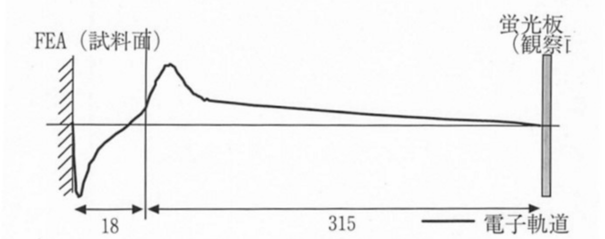


図２‐10　全体の電子軌道

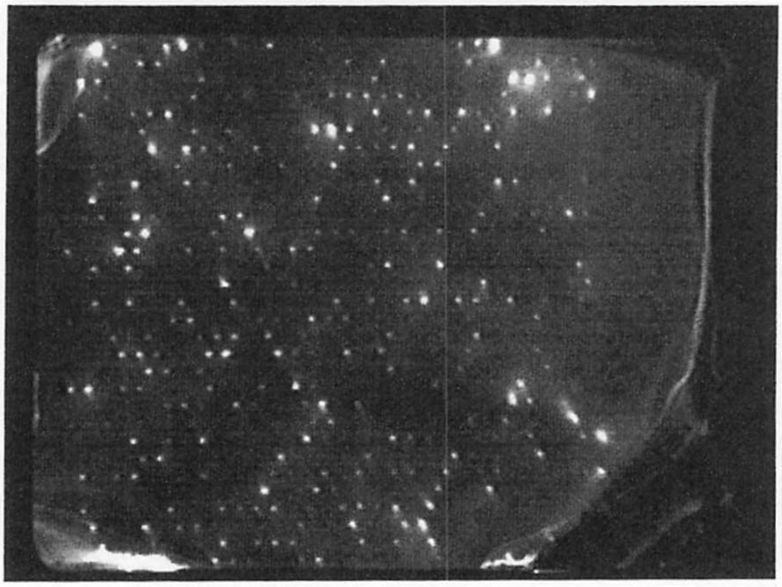
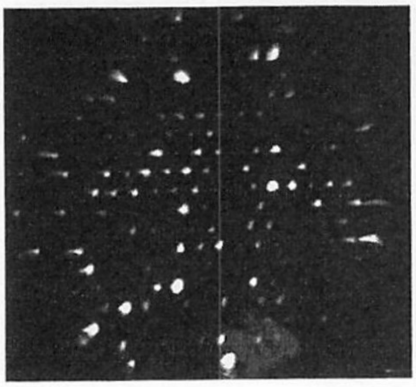
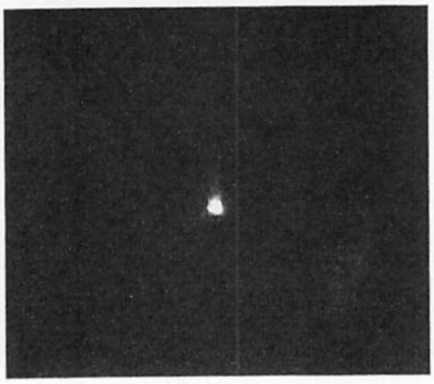


図 4－1－1　FEA 放射電子像の一例（約 300 倍）





(a)視野100μmφの球面収差　(b)視野5μmφのコマ収差

Fig.2-5　PEEMによる放射電子像に現れる収差

2002