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LETTER

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A novel method for formation of single crystalline tungsten nanotip

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Abstract

A point electron source is desired to improve performance of high brightness electron beam instruments. It is valuable to create nano-sized tungsten (W) tip from sharp ordinary polycrystalline W needle. The sharp W needle, which is manufactured by electrochemical etching, has been practically utilized as a cold field emission electron source. A novel method for formation of single crystalline W nanotip on the top of h-BN coated conventional polycrystalline tungsten, by supplying high voltage, has been found. The W nanotip with an apex radius as small as a few times 10 nm would be grown on the top of the polycrystalline W needle. Field emission characteristics of obtained W nanotip are measured, and the field emission microscopic (FEM) and transmission emission microscopic (TEM) images are observed. The emission current from the W nanotip is measured to exceed 0.1 mA. The FEM image shows significant electron emission from the crystallographic facets of the W single crystal. From these results, the present method for formation of the single crystalline W nanotip would be expected as a key technology to realize a point electron source with a nano-sized apex which makes it possible to improve the performance of high brightness electron beam instruments, especially tiny X-ray tubes for medical use, as well as a cantilever of scanning probe microscope.

Background

More than 100 years, thermal electrons emitted from heated filament have been widely utilized for any X-ray tube including medical use. Although X-ray tubes with thermal electron source would become rather huge, ones with cold field emission electron source could be constructed tiny, because of operating at room temperature, and what's more utilized to extended application to diagnosis or therapy like a fiber scope in various medical fields.

Field emission is a phenomenon of emitting electrons at room temperature by quantum mechanical tunneling effect, when we supply high electric field (more than 10^9 V/m) on a metal surface, which is illustrated in Fig. 1. Current density of the field emission J [A/cm^2] was formulated by Fowler and Nordheim [1], by using of an electric field F [V/cm] and a work function φ[eV] of the metal as follows;

$$J = \left(\frac{e^3F^2}{8\pi h\phi}\right) exp\left\{-\frac{8\pi(2m)^{\frac{1}{2}}\phi^{\frac{3}{2}}}{3heF}\right\} \tag{1}$$

where e, m, and h are elementary charge, electron mass, and Planck's constant, respectively. If an emission current I [A] is taken to AJ (A: emission area), and the electric field F is supposed to be βV (β: field enhancement factor, V: supplied voltage), we can numerically reformulate (1) as follows;

$$ln\left(\frac{I}{V^2}\right) = ln\left(\frac{1.54\times10^{-6}A\beta^2}{\phi}\right) - \frac{6.83\times10^7\phi^{\frac{3}{2}}}{\beta V} \tag{2}$$

This formula represents linear relation between $ln\,(I/V^2)$ and $1/V$. We call this Fowler and Nordheim plot, or shortly F-N plot, if ordinate and abscissa are chosen as ln (I/V^2) and $1/V$, respectively. Therefore, we call field emission is occurred when the F-N plot shows linear relation.

The field enhancement factor β [cm^{-1}] and the emission area A [cm^2] are calculated from the slope ζ and

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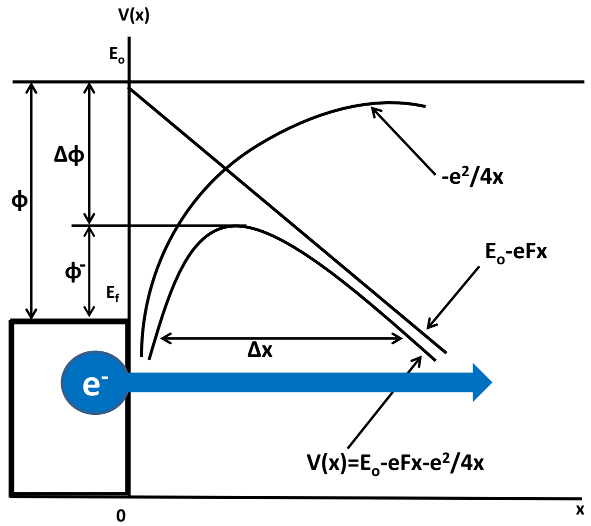


Fig. 1 Principle of field emission The mirror potential ($-e^2/4x$) is overlapped by supplying high electric field potential (–*eFx*) on a metal, which is finally responsible for reducing the surface potential barrier. Therefore, electrons in the metal can penetrate the surface by quantum mechanical tunneling effect, because of decreasing the thickness (Δ*x*) of surface potential barrier

ordinate intercept b of the F-N plot line by use of formula (2) as follows;

$$\beta = -\frac{6.83\times 10^4\times\phi^{\frac{3}{2}}}{\zeta},\quad A=\frac{\phi exp(b)}{1.54\times 10^{-6}\times\beta^2} \tag{3}$$

These formulae show that the field enhancement factor β is in inverse proportion to the slope ζ, and the emission area A is in exponential proportion to the ordinate intercept b. If we know the value of the work function ϕ of the metal, we can estimate the values of β and A from the formulae (3), through experimentally obtained F-N plot line.

Experimental equipment

Figure 2 shows apparatus of experimental equipment for field emission. The main chamber can be evacuated up to 10^{-8} Pa by TMP (Turbo Molecular Pump) and RP (Rotary Pump), not so as to be interrupted by residual gases in the chamber, when electrons are emitted from the metal surface. In case of degrading the vacuum by increasing emission current, liquid nitrogen was supplied in the server of the chamber so as to keep the vacuum of 10^{-8} Pa order.

A sample of sharp tungsten (W) needle spot-welding on a half circled W filament is mounted on normal to an anode plate, which is illustrated in upper left of Fig. 2. This shape is suitable for resistance heating in order to remove surface contamination from the sample W needle. The ordinary polycrystalline W needle has a sharp apex manufactured by electrochemical etching in 1 N KOH solution, which is shown in upper right of Fig. 2. The W needle can be linearly moved from outside of the chamber, and therefore we can easily vary the distance between the W needle and anode plate. The anode plate has also a phosphor screen, by which we can directly observe FEM (Field Emission Microscope) image from emitted electrons, out of chamber through an optical fiber plate attaching on the phosphor screen. This illustrates as a viewing port in Fig. 2. By supplying high voltage to the anode plate, emission current from the W needle can be measured by a fast current meter, by which we can continuously gather split current (repetition time is 0.2 s) through a personal computer.

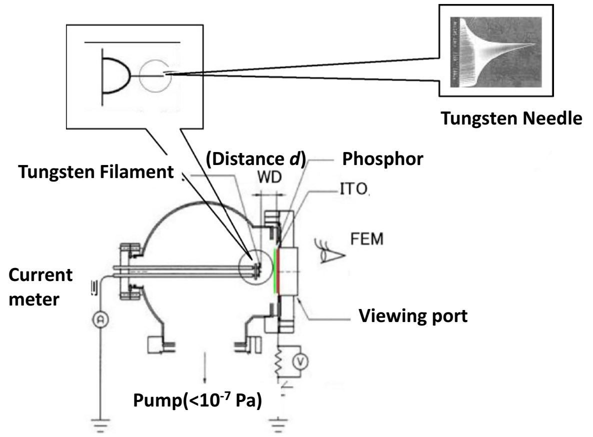


Fig. 2 Apparatus of experimental equipment for field emission

Simulation of electric field

We calculated an electric field by using a software code of electromagnetic field, ELFIN (ELF Corp.) [2]. The ELFIN code can calculate any electric field at a sharp apex with high precision by using of an original analytical integral method, not an ordinary finite element method.

Figure 3 shows a sample of calculated electric field distribution, where a sharp earthed W needle is placed perpendicular to an anode plate supplied by high voltage. The electric field at the apex of W needle was calculated as function of the distance d between the cathode and anode by the ELFIN code, which is shown in Fig. 4. We ascertained the calculated electric field as high as 10^9 V/m, where the diameter and apex curvature radius of the W needle is assumed to be 0.3 mm and 100 nm, respectively and the supplying anode voltage to be 1000 V. This variation curve shows that calculated electric field at the sharp W needle apex is extremely

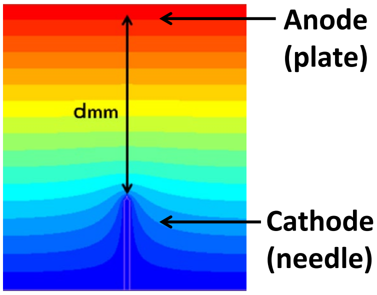


Fig. 3 Calculated electric field distribution between the cathode and anode

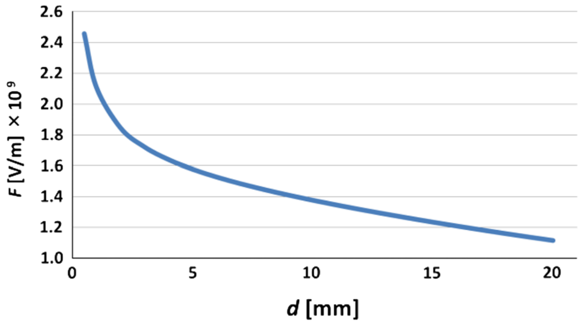


Fig. 4 Variation of calculated electric field at the W needle apex with the distance *d* between cathode and anode

increased below 3 mm of the distance *d*, although gradually decreased over 3 mm.

Experimental results

Field emission from sharp polycrystalline W needle

Figure 5 shows voltage-current characteristics obtained from field emission from a sharp ordinary polycrystalline W needle manufactured by electrochemical etching as mentioned above. Each curve is corresponding to variation of the distance *d* between the cathode W and anode plate. This represents that the threshold voltage to start field emission is increased, as the distance *d* is increased. It is readily recognized from decreasing the supplied electric field as increasing the distance *d*.

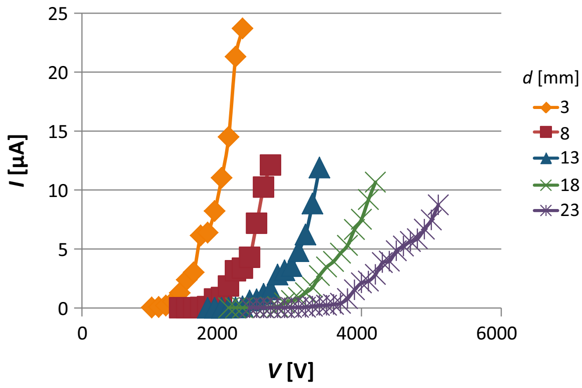


Fig. 5 Voltage-current characteristics emitted from the sharp ordinary polycrystalline W needle

Figure 6 shows variation of the F-N plot versus the distance *d,* which is derived from the experimental results in Fig. 5 by use of above formula (2). These F-N plots are likely to have linear relation for any distance *d.* This shows that field emission is occurred at room temperature by supplying high voltage in case of the sharp ordinary polycrystalline W needle. Table 1 shows variation of β [cm^{-1}], r [cm], and A [cm^2] versus the distance *d* calculated from the F-N plots through the formulae (3), where the curvature radius r is assumed to be $1/(5\beta)$ [3]. These values of β and r are reasonable on account of the sharp ordinary polycrystalline W needle. The field enhancement factor β is increased, as the distance *d* is decreased. Therefore, the curvature radius r is decreased, as the distance *d* is decreased. This means that the field emission electrons tend to emit only from the most top of the sharp W needle apex, as the distance *d* is decreased. This tendency corresponds to the calculated electric field, which shows extreme increase as decreasing the distance

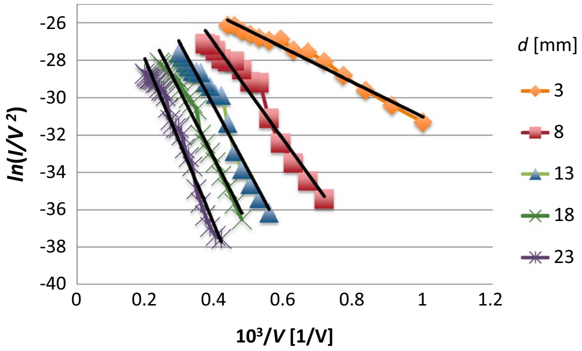


Fig. 6 Variation of F-N plots from the sharp ordinary polycrystalline W needle with the distance *d* between the cathode and anode

Table 1 Variations of β [cm^{-1}], r [cm], and A [cm^2] with distance *d* between the cathode and anode calculated from the F-N plots in Fig. 6

d [mm]	β [cm^{-1}]	*r* [cm]	*A* [cm^2]
3	7.11E+04	2.81E−06	1.83E−13
8	2.53E+04	7.92E−06	2.17E−10
13	1.89E+04	1.06E−05	4.02E−10
18	1.78E+04	1.12E−05	6.48E−11
23	1.47E+04	1.36E−05	6.04E−11

d. On the contrary, the emission area *A* is fluctuated on the distance *d*. The reason is not sure at the present time.

Field emission from sharp W needle coated with h-BN thin film

Hexagonal boron nitride (h-BN) is well known to have layered structure binding with van der Waals force like graphite as shown in Fig. 7. Nevertheless, h-BN is an insulator unlike graphite. We had tried to improve field emission characteristics by coating with h-BN thin film on various materials [4–6]. We coated the h-BN thin film on the W needle at a substrate temperature of 350 °C, by an ion plating method with Ar and N_2 gases in electron bombardment on B source.

We carried out similar field emission experiments by using the W needle coated with h-BN thin film. Figure 8 shows the results of experimentally obtained F-N plots, which are also likely to have linear relation for three thicknesses (200, 300 and 500 nm) of h-BN thin film. These also show that field emission is occurred at room temperature in case of the W needle coated with any thickness of h-BN thin film. Furthermore, we found that an extremely sharp and straight W apex was grown up in the W needle coated with thickness of 500 nm h-BN thin film. On the contrary, curved W apexes were grown up in the W needle coated with thickness of 200 or 300 nm h-BN thin film. The reason of growing up curved W needle apexes coated with thickness of 200 or 300 nm h-BN thin film is not clear, but the thinner h-BN thin film would be influenced by supplying high electric field. These SEM (Scanning Electron Microscope) images of the W needle apexes with h-BN thin films are shown in inserts of Fig. 8.

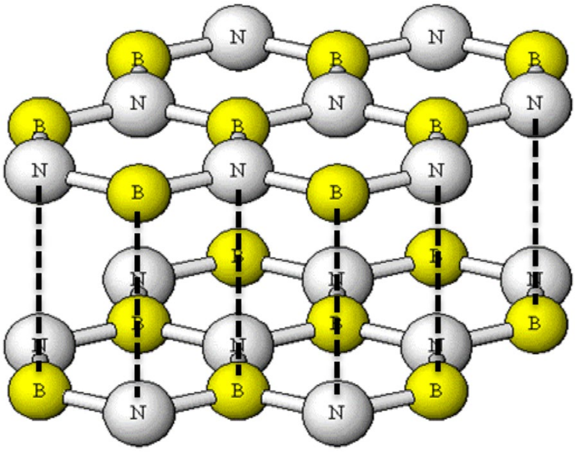


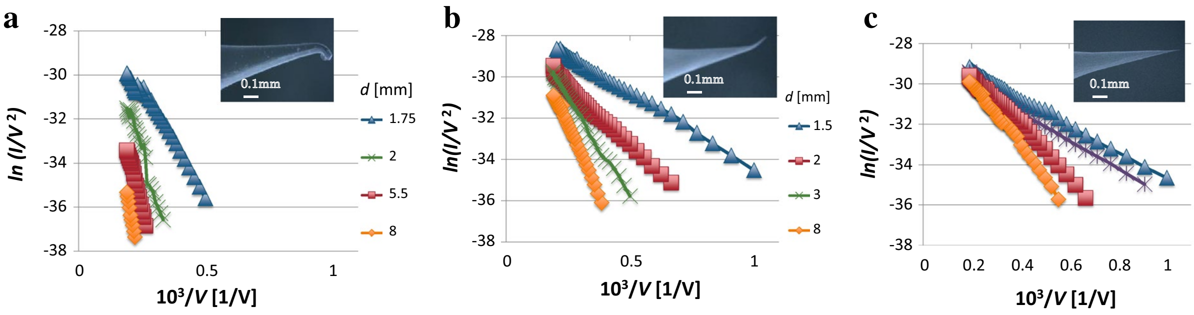
Fig. 7 Model of atomic structure of h-BN (hexagonal born nitride)

FEM image of W needle coated with h-BN thin film

Figure 9 shows FEM image emitted from the W needle coated with 500 nm h-BN thin film, in which the h-BN thin film is blown up in some way. The FEM image shows formation of crystallographic facets of single crystalline W apex.

TEM image of W needle coated with h-BN thin film

Figure 10 shows TEM (Transmission Electron Microscope) image emitted from the W needle coated with 500 nm h-BN thin film. The black and light gray areas of the TEM image would correspond to W and h-BN, respectively. The curvature radius of the topmost tungsten is a few times 10 nm. Furthermore, the topmost TEM picture of Fig. 10, as shown Fig. 11, indicates clearly atomic image. We plan to carry out future experiments to determine precisely the orientation of the single crystalline W. In any case, the extreme sharp apex seems to grow on the top of ordinary polycrystalline W needle. The formation mechanism is not well known, but the reason why blowing up the h-BN thin film and creating the single crystalline W apex is surely caused by supplying high electric filed on the W needle. Especially, h-BN



h-BN:200nm h-BN:300nm h-BN:500nm

Fig. 8 Variation of F-N plots with thickness of h-BN thin film as well as the distance *d* between the cathode and anode. *Inserts* show SEM images of the W needle apexes. **a** h-BN:200nm, **b** h-BN:300nm, **c** h-BN:500nm

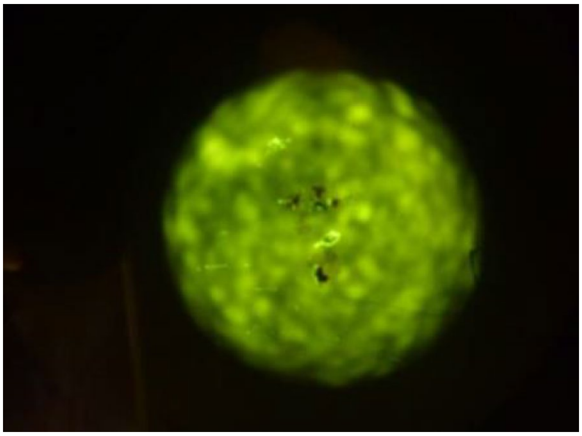


Fig. 9 FEM image of the W needle coated with 500 nm h-BN thin film after carrying out field emission experiment

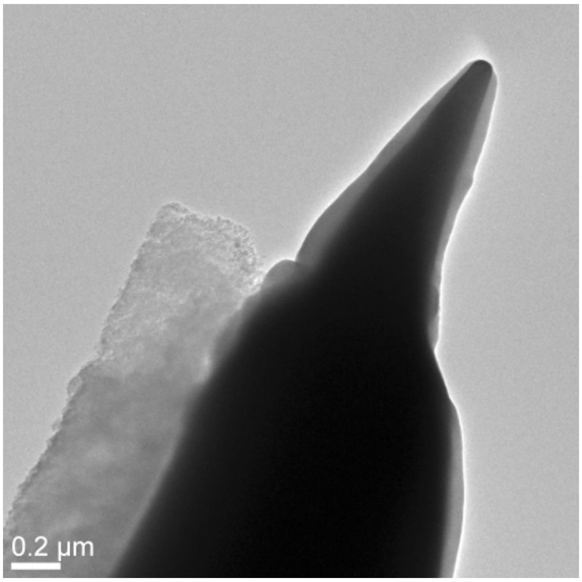


Fig. 10 TEM image of the W needle coated with 500 nm h-BN thin film after carrying out field emission experiment

thin film must be easily blown away from the substrate W needle apex because of the layered structure.

One proposed process to create the single crystalline W nanotip is as follows. First, electro migration in ordinary polycrystalline W needle was occurred by supplying high electric field. Secondly, a small migrated chip in the W needle was penetrated into the h-BN thin film by supplied high electric force. Thirdly, sudden large current was flown from the W needle chip, and the chip was partially heated by field emission current. Finally, the h-BN thin film was blown up by the extreme large current and the chip would grow a single crystalline W nanotip under the high electric field.

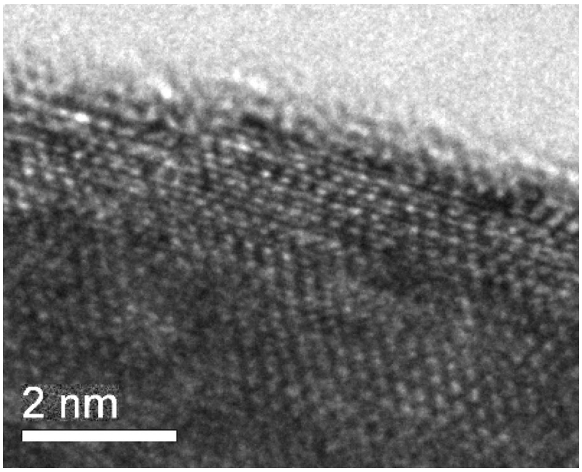


Fig. 11 TEM image from the apex of Fig. 10, shows clearly atomic structure of the single crystalline W nanotip

At last, we express that we cannot find such FEM images of single crystalline W with thickness of 200 or 300 nm h-BN thin film, which could not be explained by now. It would be related to formation of the curved apexes of the W needle with thickness of 200 or 300 nm h-BN thin film.

Conclusion

We will make a summary of this article as follows;

(1) We confirmed field emission at room temperature by supplying high voltage from sharp ordinary polycrystalline W needle, which was manufactured by electrochemical etching.
(2) We compared calculated electric field with the field enhancement factor β and the emission area A, which were obtained from F-N plots through field emission experiment, in order to elucidate precisely the mechanism of field emission. We confirmed that the field emission electrons emitted only from the most top of the sharp W needle.
(3) We could create the W nanotip with an extremely sharp apex, under carrying out field emission experiment for ordinary polycrystalline W needle coated with h-BN thin film. And we ascertained the W needle coated with thickness of 500 nm h-BN thin film to grow up an extremely sharp no-curved apex and to show formation of single crystalline W from the FEM and TEM images. The emission current from the W nanotip is measured to exceed 0.1 mA.

(4) We proposed one mechanical process to create the single crystalline W nanotip by supplying high electric field. In near future, we will confirm the formation mechanism of single crystalline W, by observing diffraction patterns of X-ray or electron beam. The created W nanotip would be applied to realize high brightness electron point source which makes it possible to improve any electron beam instruments, including tiny X-ray tubes for medical or industrial use, as well as a cantilever of scanning probe microscope.

Authors' contributions

SH conceived of the study, and participated in its design and coordination and helped to draft the manuscript. MO, ST and HN carried out the experiments, and summarized the data. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

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