PAPER • OPEN ACCESS

Stable and environment-hard vacuum nanoelectronic devices for aerospace applications

Stable and environment-hard vacuum nanoelectronic devices for aerospace applications

M Nakamoto[*] **and J Moon**

Graduate School of Integrated Science and Technology, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu, Shizuoka 432-8011, Japan

*E-mail: nakamoto.masayuki@shizuoka.ac.jp

Abstract. Extremely stable field-emitter arrays (FEAs) having low work function as well as resisting harsh environments have been prepared by the transfer mold emitter fabrication method to make remarkably resistant and low operation-voltage vacuum nanoelectronic devices in harsh environments such as a strong radical atmosphere. Amorphous carbon and titanium nitride, which have a low work function as well as an environmental hardness, were used as the emitter material. The current emission fluctuations of amorphous carbon FEAs having no resistive layers, were as low as ±1.7%, (the lowest ever reported value), as compared to 5–100% of general FEAs fabricated by the conventional method and containing resistive layers. The amorphous carbon FEAs show the most stable emission characteristics, as compared to transfer mold FEAs coated with titanium nitride or platinum (Pt), because amorphous carbon FEAs have the most uniform tip radii. The amorphous carbon FEAs exhibit stable fluctuations of less than ±5.1% under in situ oxygen radical treatment. Panel and pixel electric thrusters have been proposed that use transfer mold FEAs. These electric thrusters make it easy to produce large and small thrusters. transfer mold amorphous carbon FEAs can be used to create highly efficient and reliable vacuum electronic devices such as electric propulsion engines and field-emission displays.

1. Introduction

Low operation-voltage field emitter arrays (FEAs) for extremely stable vacuum nanoelectronic devices, can be realized by using low-work function emitter materials and unique emitter fabrication method, that is also referred to as the transfer mold emitter fabrication method (TMEFM)[1–3]. This method produces sharpened emitter arrays uniformly and reproducibly.

However, FEAs are often exposed to high temperature environments and highly oxidizing atmospheres during the vacuum sealing or fabrication process of field emission displays (FEDs).

Besides, electrodynamic tethers (EDT) in a low-earth orbit (LEO) above 80–500 km has to undergo an exceedingly reactive oxygen-radical atmosphere. An EDT system, which is one kind of a spacecraft or a satellite, is comprised of 5 km–long conductive wire having electron emitters and collectors at both ends. It can be used for propulsion, stabilization or maintaining the trajectory of space spacecraft in orbit. Electrons were emitted from electron emitters at a spacecraft to space, while electrons were gathered by electron collector from space. Space in LEO has electrons and ion species having densities of about 1×10^6 cm^{-3} [4]. If currents along the tether flow because of electric circuit formed by electron emitters, tether and electron collectors, the spacecraft or the satellite exert a Lorentz force against a magnetic field of Earth and can move. FEAs have the advantage that they require no fuel and warm-up

time. Therefore, FEAs are suitable for an EDT.

However, one of the major issues is the degradation due to the harsh environments of FEAs in EDTs, because FEAs may be directly exposed to highly reactive environments such as oxygen radicals. Thus, evaluation of field emission characteristics during the exposure of highly reactive atmosphere such as in-situ oxygen radical treatment is necessary to realize reliable and stable electric propulsive system even in a highly reactive atmosphere. An electrical propulsion system, e.g., ion engines having advantages of very high fuel efficiency, can preserve impellent forces for long periods.

New ion engines as space propulsion systems by using an assembly of transfer mold field emitter arrays, were proposed in our previous report, can be useful to spacecraft applications [2].

2. Experimental methods

Figure 1 shows the fabrication process for FEAs by using the transfer mold method array.

FEAs were fabricated by using the transfer mold emitter fabrication method, which has various types such as Si mold-type method and coated type method [1–3]. Substrates of silicon mold were prepared by anisotropic etching of silicon using potassium hydroxide (KOH) aqueous solutions to form pyramidal holes (mold) having a very sharp vertex in figure 1(a).

Silicon dioxide layer was made by thermal oxidization method in Si substrate mold to obtain the intrinsic sharpening of emitter-tips in figure 1(a). The 20 nm-thickness amorphous carbon thin film as an emitter material, was deposited inside a Si mold formed by a thermal SiO_2 layer in figure 1(b).

The deposition of amorphous carbon thin film was carried out by using a plasma-enhanced chemical vapor deposition method with mixed gases of acetylene and argon at room temperature. Next, Ni as the supporting layer was filled in the remaining volume of the mold after the deposition of amorphous carbon thin film by using the sputtering method in figure 1(c). Then, mold and glass substrate were bonded by the anodic bonding method in figure 1(d). The elimination of Si Mold substrate and silicon dioxide film by using a tetramethylammonium hydroxide solution and a buffered hydrofluoric acid solution, respectively, is shown in figure 1(e). Then, amorphous carbon FEAs by TMEFM can be obtained.

The coated-type transfer mold emitter-fabrication method was described as follows. Ni was firstly filled by electroplating method in Si mold as shown in figure 1(b*). Mold and glass substrates were bonded by using the anodic bonding method in figure 1(c*). After the elimination of Si Mold substrate and silicon dioxide film, the coated-type TiN-FEAs or Pt-FEAs have been fabricated by titanium nitride or platinum coating on Ni FEAs using radio-frequency sputtering of TiN or Pt thin film in figures 1d and 1e [3].

For the evaluation of emitter-tip morphology for transfer mold, 30 images of FEAs on the random positions of all FEA segment area were taken by using high-resolution FE-SEM with the magnification of 650,000. Then, the average values of tip radius and their standard deviations were statistically estimated. The morphology and emission characteristics amorphous carbon were evaluated among those of TiN coated type FEAs and Pt-coated type FEAs.

According to the UPS results, titanium nitride and amorphous carbon thin film can withstand harsh environments and have as low as work functions of 3.2 eV and 3.6 eV, compared with those of 5.0 eV for multiwalled carbon nanotubes (CNTs). The results were compared with those of platinum-FEAs (5.1 eV); such FEAs do not have a low work function but can withstand harsh environments.

The morphology such as tip radius and base length of field emitter arrays was evaluated by using a field-emission scanning electron microscope (FE-SEM). transfer mold field emitter arrays have a pyramidal shape with the average base length of 1.6 μm, the pitch of 3.2 μm and the emitter height of 1.1 μm. The transfer mold FEAs had been fabricated by using the 6-inch Si wafer and been patterned by the FEAs having a segment of 4×4 pieces. The FEA area of one segment was $1.5 \times 1.5 \ cm^2$. The uniform morphology of all FEAs for all segments on the 6–inch size substrate had been evaluated by using FE-SEM. Then, one segment FEAs of $1.5 \times 1.5 \ cm^2$ was cut and was carried out emission current-electric field measurements. Anode electrode having the hemispherical shape with the diameter of 1 mm was located on the emitter array at a spacing of 10 μm. Field emission

measurements were carried out at the random positions of the emitter area.
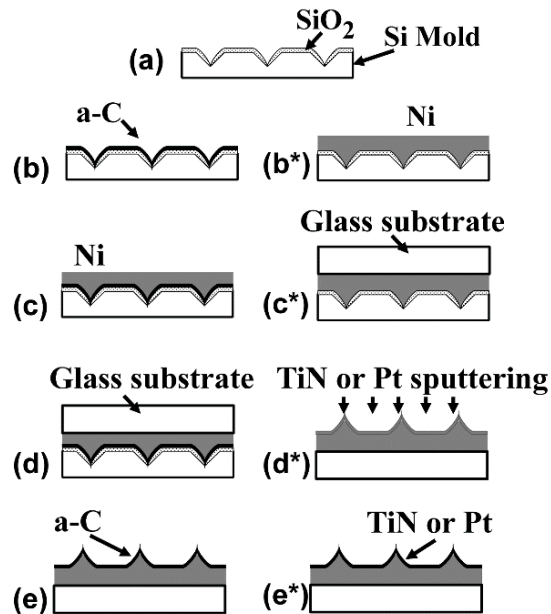
Figure 1. The fabrication process for FEAs by using transfer mold method.

The uniformity of field emission has been confirmed by measurement of all positions and segments FEAs on the 6–inch size substrate. I–V measurements were performed under vacuum conditions of 3.8×10^{-9} Torr without oxygen radical treatment and 7.5×10^{-7} Torr during oxygen radical treatments, respectively. Values of turn-on fields were defined with bias voltages at the condition of 10-μm-separation between anode and cathode and the 10 nA emission current.

The field-emission characteristics during in-situ oxygen treatment were evaluated by using the I–V measuring vacuum system with the oxygen radical source [2].

The flux of oxygen radical was 10^{15} atoms/cm^2·sec, which is as high as 10^7–10^8 times ordinary fluxes in the LEO (about 10^7–10^8 atoms/cm^2·sec) [4]. Work functions and chemical properties were estimated with ultraviolet photoelectron spectroscopy (UPS) and x-ray photoelectron spectroscopy (XPS).

3. Results and Discussion

Figure 2 shows FE-SEM images of amorphous carbon FEAs, TiN-FEAs, and Pt-FEAs fabricated by TMEFM, as well as their tips with and without treatment. Figures 2(a), 2(b), and 2(c) depict the amorphous carbon FEAs, TiN-FEAs, and Pt-FEAs, without treatment.

Tip radii of TiN-FEAs, amorphous carbon FEAs and Pt-FEAs were equal 6.8, 7.8, and 10.3 nm, respectively. Values of 6.8-10.3 nm are approximately equal or somewhat smaller than the diameter of multiwalled CNTs (5–10 nm). Moreover, amorphous carbon FEAs, TiN-FEAs, and Pt-FEAs had tip radii's standard deviations of 1.5, 1.9, and 2.0 nm, respectively.

Therefore, the FEAs fabricated by the ransfer mold method, are very uniform, unlike nonuniform tip radii, and are different in height and pitch from typical FEAs, e.g., carbon nanotube FEAs (CNT FEAs). Moreover, the amorphous carbon FEAs have the highest uniformity compared with those of TiN-FEAs and Pt-FEAs. RF sputtering method was used to prepare TiN-FEAs or Pt-FEAs by TiN thin film coating or Pt thin film coating on Ni FEAs. transfer mold amorphous carbon FEAs was prepared by the Si mold-type TMEFM having very sharp corners due to the intrinsic tip sharpening. Therefore, amorphous carbon FEAs have uniform tip-morphology.

The average values of tip radii for TiN-FEAs, amorphous carbon FEAs and Pt-FEAs, were 7.0, 8.0,

and 10.5 nm, respectively, after 12-min radical treatment. Tip radii were approximately equal regardless of oxygen treatment.
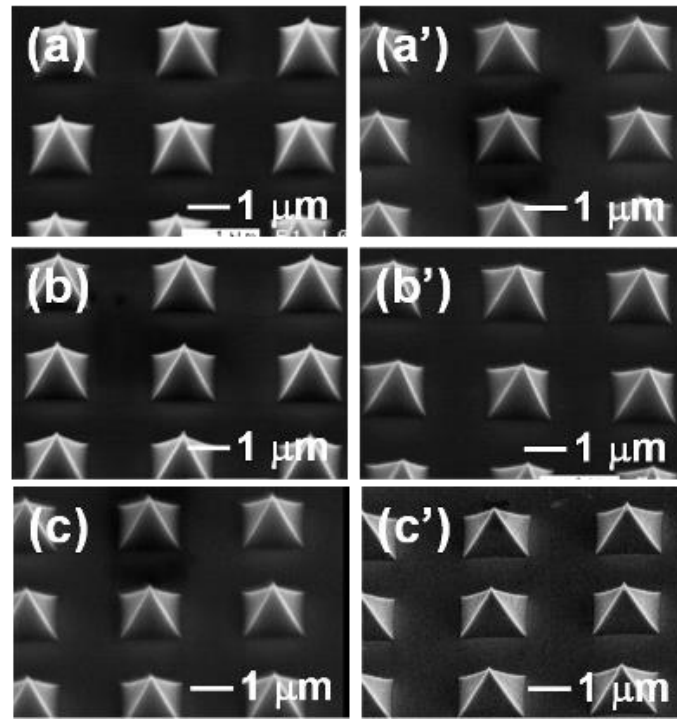

Figure 2. FE-SEM images about transfer mold FEAs and their tips. (a) Amorphous carbon FEAs without treatment; (a') Amorphous carbon FEAs with treatment for 12 min; (b) TiN-FEAs without treatment; (b') TiN-FEAs with treatment for 12 min; (c) Pt-FEAs without treatment, (c') Pt-FEAs with treatment for 12 min.

No damages of emitter tips for amorphous carbon FEAs, TiN-FEAs and Pt-FEAs occurred due to the radical treatment.

The amorphous carbon thin film has anticorrosive and solid properties, as well as low work-function compared with 4.3–4.5 eV of the common emitter materials such as molybdenum [5]. In this work, the work function (3.6 eV) of the amorphous carbon film was estimated by using UPS. According to our experimental XPS results, the sp^3 content of amorphous carbon on the emitter surface of amorphous carbon FEAs by TMEFM was analyzed to be 85.6%, estimated from the $sp^3/[sp^3+sp^2]$ ratio by using deconvolution of the XPS spectra concerning sp^3 and sp^2 peak. Amorphous carbon films have high elastic moduli of 55-143 GPa under condition of sp^3 contents higher than 60% [6]. Therefore, chemically inert amorphous carbon film having low hydrogen content and defect states can be achieved with high sp^3 contents of more than 60%.

Figures 3(a) and 3(b) show the relation between emission currents and electric fields, and Fowler-Nordheim (F-N) plots. Turn-on fields of TiN-FEAs, amorphous carbon FEAs, and Pt-FEAs were as low as 15.4, 17.5, and 27.1 V/μm, respectively.

Some research results were reported on turn-on field values of 2.8–3.6 V/μm for ultra-nanocrystalline diamond FEAs with no description of anode-to-emitter distance [7], 1.1–1.2 V/μm for CNT FEAs with 2-mm anode-to-distance and work function of 5 eV, 3.5 V/μm for CNT FEAs with 1.8 mm anode-to-distance [8-9]. However, in agreement with the quantum mechanics, even under the nanoscale tip radii and electrode separation, to leave electrons from Fermi energy level to the vacuum energy level, one must assume that their energy level is between the Fermi level and the vacuum level, which implies the work function of emitter materials.
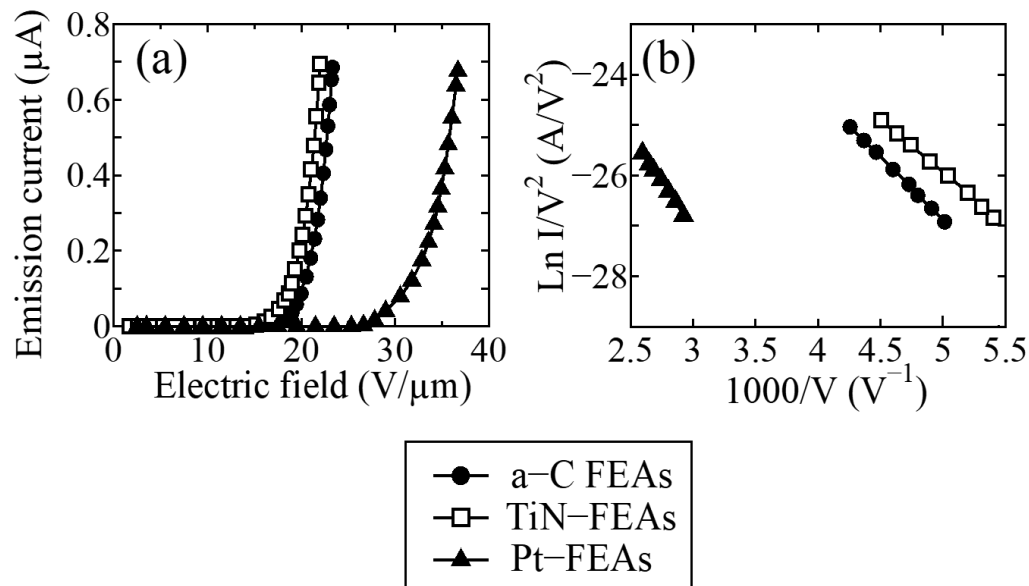
Figure 3. (a) Relation between emission current and electric fields, and (b) F-N plots of amorphous carbon FEAs (a-C FEAs), titanium nitride-FEAs (TiN-FEAs), and platinum-FEAs (Pt-FEAs).

The turn-on E-field with a larger work function is required. Even though the turn-on E-field of field emitters with a substance having work function of 5 eV, is as low as 1 V/μm in the condition of 1 mm anode-emitter separation (also referred to as electrode separation) and the biased voltage of 1 kV, the turn-on E-field should increase from 1 V/μm at 1 mm electrode separation. Then, the biased voltage has to be higher than 5 V so that the turn-on E-field is required with higher than 50 V/μm in the condition of 0.1 μm electrode separation. Usually, the turn-on E-fields under condition of 1–2 mm electrode separation, can be reduced to 100–300 μm.

However, the gradual increase of turn-on E-fields occurs in the range of less than 100–300 μm electrode separation. Turn-on E-fields enormously increase in the range of less than 10–30 μm electrode separation.

Thus, this electrode separation is one of the most critical parameters to compare and evaluate the performance of FEAs and must be mentioned. However, many reports indicate that electric fields of less than work function values per micrometer such as 1–4 V/μm, do not clarify the electrode separation such as anode-to-cathode distance or circumscribe the range of relatively long electrode separation, e.g., 100 μm to 2 mm. If the gated transfer mold FEAs for vacuum nanoelectronic devices are considered, the separation between emitter cathode and the gate electrode of fewer than 10 μm is significant for the I-V measurement. Considering 4.5 eV of Mo work function, the turn-on voltage of molybdenum FEAs by TMEFM is 7 V, which is nearest to the theoretically lower limit turn-on voltage of 4.5 V [1]. The turn-on field is 17.5 V/μm, which is approximately estimated regarding the gate-to-emitter separation of 0.4 μm. Therefore, the values of 15.4–27.1 V/μm are as low as those of typical FEAs like Spindt FEAs and CNT FEAs, which have 50−600 V/μm, approximately estimated as the condition of a short anode-to-emitter separation of less than 30 μm [10–15].

TiN-FEAs showed lower turn-on fields than those of amorphous carbon FEAs and Pt-FEAs, because TiN-FEAs with smaller tip radius, exhibited higher geometric factors than those of amorphous carbon FEAs and Pt-FEAs. The relevant parameters in the Fowler−Nordheim (FN) field-emission theory are the geometric factor (β) which can be estimated by the emitter's microstructure geometry, and the work function (φ) [2, 3].

Martin et al. [16] showed that the β factor (β_1) in the range of $D \gg r$, can be approximately calculated as (1). D is anode-to-emitter tip separation, and r is the emitter-tip radius.
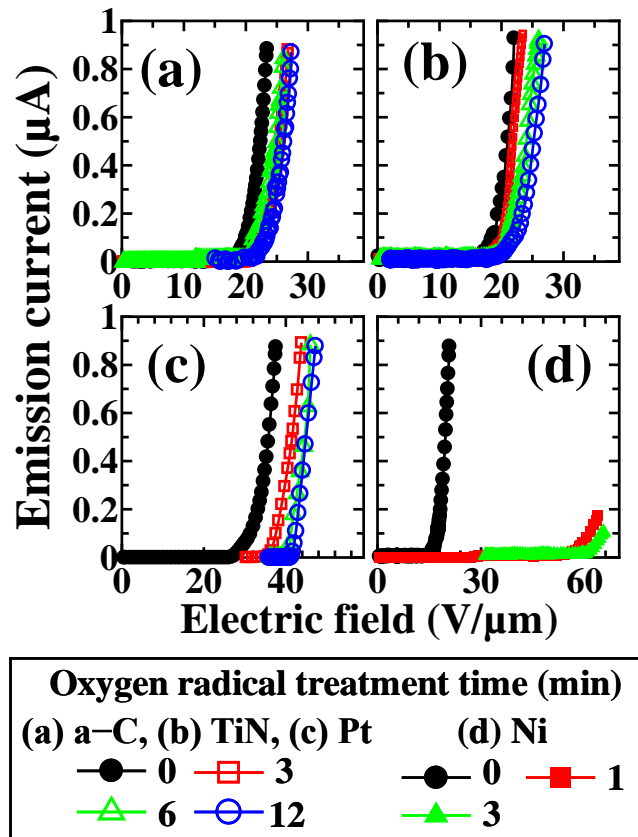
Figure 4. The relation between emission current and electric field for (a) amorphous carbon FEAs, (b) TiN-FEAs, (c) Pt-FEAs and (d) Ni-FEAs depending on the radical treatment time.

The β_1 can be approximated by

$$\beta_1 = 2\left[r\ln\left(4D \cdot r^{-1}\right)\right]^{-1}. \tag{1}$$

In our experiment, D is 10 μm and $r = 6.8$–10.5 nm. The value of D is 950–1470 times larger than the values of r. Therefore, (1) can be applied for evaluation of geometric factor.

Charbonnier et al. [17] approximated the β factor (β_2) as

$$\beta_2 = 1.4 \cdot \left[r^{2/3}D^{1/3}(\tan\theta)^{0.2}[(D+h)\cdot h^{-1}]^{1/2}\right]^{-1}, \tag{2}$$

where θ is a half curvature-angle at an apex of emitter tip, r is an emitter-tip radius, D is an anode electrode-to-emitter separation, and h is a height of emitter. The experimental values of the geometric factor from F-N plots slope are given by

$$\beta_{ex} = 6.5 \times 10^7 \cdot m^{-1} \cdot \varphi^{3/2}, \tag{3}$$

where φ is the emitter materials' work function, and m is the F-N plot slope.

Using (1), β_1 was found to be 3.04×10^7 cm^{-1}, 3.44×10^7 cm^{-1} and 2.38×10^7 cm^{-1} for amorphous carbon FEAs, TiN-FEAs, and Pt-FEAs, respectively. Using (2), β_2 was 0.62×10^7 cm^{-1}, 0.68×10^7 cm^{-1} and 0.52×10^7 cm^{-1} for amorphous carbon FEAs, TiN-FEAs, and Pt-FEAs, respectively. Using (3) and the work function found with UPS, β_{ex} were 1.51×10^7 cm^{-1}, 2.31×10^7 cm^{-1} and 1.50×10^7 cm^{-1} for amorphous carbon FEAs, TiN-FEAs, and Pt-FEAs, respectively. The 3.6 eV, 3.2 eV and 5.1 eV of work functions for amorphous carbon, titanium nitride, and Pt, were obtained by the UPS

measurement.
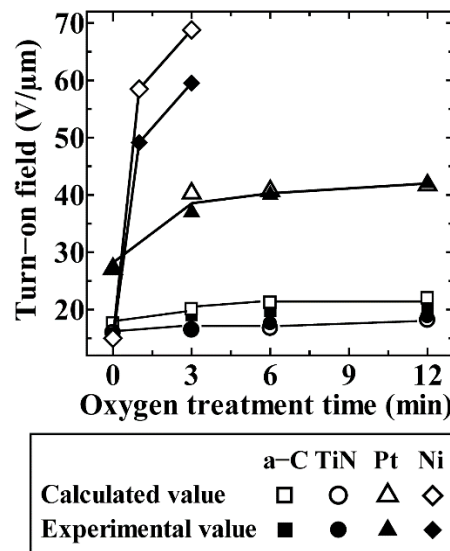
Figure 5. Calculated values and experimental values of turn-on fields depending on radical treatment time for amorphous carbon FEAs, TiN-FEAs, Pt-FEAs, and Ni FEAs.

Figure 4 shows emission current-electric fields characteristics of amorphous carbon FEAs, TiN-FEAs, and Pt-FEAs, depending on the radical treatment time. Turn-on field of 14.9 V/μm for Ni FEAs before in-situ radical treatment, increased approximately fourfold to 59.4 V/μm after 3-min oxygen radical treatment and even arcing was happened after a 3-min-radical treatment.

Turn-on fields for the amorphous carbon FEAs, TiN-FEAs, and Pt-FEAs were varied as small as 17.5 to 21.8 V/μm, 15.4 to 18.8 V/μm, and 27.1 to 42.1 V/μm, respectively. It means that FEAs with having amorphous carbon, TiN and Pt as emitter materials, possess more stable field emission characteristics even in highly oxidizing environments.

Besides, turn-on fields for Pt-FEAs were higher than those of TiN-FEAs and amorphous carbon FEAs because the tip radii of Pt FEAs were larger. Pt-FEAs had a smaller geometric factor (2.38×10^7 cm^{-1}) than those of TiN-FEAs (3.04×10^7 cm^{-1}) and amorphous carbon FEAs (3.44×10^7 cm^{-1}).

The amorphous carbon FEAs and TiN-FEAs have as low turn-on fields as 17.5 V/μm and 15.4 V/μm, which were estimated with 10-μm anode-to-emitter separation. This is compared with 50–600 V/μm for conventional FEAs. Thus, FEAs fabricated by TMEFMcan be used in vacuum nanodevices. Moreover, the amorphous carbon FEAs have the most stable turn-on fields even though highly oxidizing environments.

Figure 5 shows turn-on field, which was estimated by the FN equation with geometric factors, where we have used (1), and work functions, where we measured by UPS results, concerning radical treatment time.

The experimental values of turn-on fields almost coincide with the theoretical values of turn-on fields about amorphous carbon FEAs, TiN-FEAs and Pt-FEAs, because geometric factors of these FEAs do not change with oxygen radical treatment.

According to our experimental XPS results, amorphous carbon FEAs exhibited as small as the peak-area ratio of 6.3%, which was estimated with oxidized portions at the XPS spectra, compared with those of 11.8% of TiN-FEAs. Besides, C$_{1s}$ peak at 285.3 eV does not shift for amorphous carbon FEAs with 12 min-oxygen radical treatment [18]. However, TiN 2p$_{1/2}$ peak of TiN-FEAs, shift from 464.6 eV to lower energy level of 464.6 eV with 12 min-treatment [19]. Ti–O bonds at the surface of TiN-FEAs have increased by oxygen radical treatment so that Ti-N bonding peak shifts due to increasing amount of oxidized matters. Thus, it can be explained that amorphous carbon FEAs can

maintain more stable field-emission characteristics in highly oxidizing environments than those of TiN-FEAs.

However, nickel (Ni) FEAs have a very intense Ni–O peak in the range of 853.5–857 eV binding energy with the radical treatment. NiO peak-area ratio was increased by 7.1 times (5.5% to 39.0%) by a 3-min radical treatment. Ni $2p_{1/2}$ peak shifted with 0.9 eV from 870.3 eV to 871.2 eV after 12-min radical treatment. Ni–O bonds at the surface of Ni-FEAs were significantly increased by the oxygen radical treatment so that Ni $2p_{1/2}$ peak shift occurred due to the increasing amount of oxidized matters. Thus, it can be explained that Ni-FEAs cannot maintain stable field emission characteristics in highly oxidizing environments. Then, turn-on fields of Ni-FEAs, as shown in figure 5, were rapidly changed.

According to work function, experimentally measured by UPS spectra, the work function of 4.5 eV for Ni FEAs were changed to 6.0 eV after 3-min treatment. Measured φ by UPS for amorphous carbon FEAs of 3.6 eV, TiN-FEAs of 3.2 eV and Pt-FEAs of 5.1 eV, varied to 3.9 eV, 3.5 eV, and 5.2 eV, respectively, after 12-min treatment. The amorphous carbon FEAs, TiN-FEAs, and Pt-FEAs have the endurance to harsh environments. Moreover, FEAs fabricated by TMEFMare very uniform in the morphology so that the calculated values of work function, coincide with the measured values.

Usually, conventional field emitter arrays have severe geometrical nonuniformity so that those FEAs with resistive layer, exhibit as high emission-current fluctuations as 5–100%. Moreover, those FEAs with no resistive layer, exhibit and several hundred % emission-current fluctuations. According to the Fowler–Nordheim theory, the calculated work function is originated from the slope of the *FN* plot derived from the I–V characteristics. The slope of *FN* plot itself is ambiguous because emissions current has significant fluctuations.

Besides, geometric factors, which can be obtained by *FN* plots, usually, cannot express correct values, because of the high fluctuation of emission currents. The high fluctuations are originated from nonuniform geometrical morphology. Therefore, the calculated work function for the conventional FEAs cannot be expressed by a reliable value.

Besides, in the case of FEAs fabricated by transfer mold method, the geometric factor can express the true values because of stable emission currents having low fluctuation. These small fluctuations are originated from remarkably uniform geometrical morphology so that work functions obtained by the true slope of *FN* plots, can express the reliable value. In conclusion, for transfer mold FEAs, the value of theoretically calculated work function coincides with those of the measured work function.

However, in the case of Ni FEAs, the calculated work functions did not correspond with the measured ones because of unreliable values due to unstable emission characteristics and arcing formation.

According to the surface analysis with XPS, in case of amorphous carbon FEAs and TiN-FEAs, C–O peak at 285.5 eV and Ti–O peak at 455 eV, respectively, were not shown with oxygen radical treatment. Besides, Pt-FEAs have no oxide peaks after radical treatment. No oxidized matters at the surface of emitters can explain keeping work functions or stable emission characteristics in highly oxidizing environments. However, in the case of Ni FEAs, a dominant peak of NiO was shown at 857.2 eV. Thus, it can be explained that Ni-FEAs cannot maintain stable field emission characteristics in highly oxidizing environments. Then, turn-on fields of Ni-FEAs in figure 5, were rapidly changed.

Figure 6 shows the emission-current fluctuations of (a) amorphous carbon FEAs, (b) TiN-FEAs, and (c) Pt-FEAs, and (d) Ni FEAs depending on in-situ oxygen radical treatment. Usually, FEAs fabricated by using typical methods, e.g., Spindt-type FEAs and CNT-FEAs, exhibit as high as 5-100% fluctuations with the resistive layer, and more than 100% fluctuations with no resistive layer.

Table 1 shows the emission fluctuations of amorphous carbon FEAs, TiN-FEAs, Pt-FEAs, and Ni FEAs depending on radical treatment. Those FEAs have no resistive layers. Those emission fluctuations were as low as values of ±1.7, ±2.5, and ±2.5%. Moreover, ±1.7% is one of the weakest fluctuations being ever reported.

No deformation of emitter tips for amorphous carbon FEAs, TiN-FEAs, and Pt-FEAs happened by the oxygen radical treatment. After field emission measurements during 30 min, those of amorphous carbon FEAs, TiN-FEAs, and Pt-FEAs were 8.0±2.0, 7.2±2.2, and 10.4±2.2 nm, respectively.
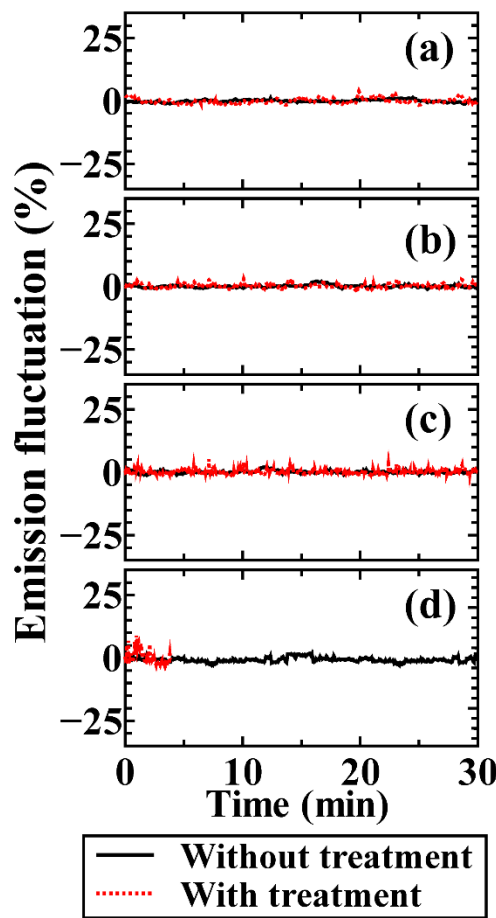
Figure 6. Emission fluctuations of (a) amorphous carbon FEAs, (b) titanium nitride-FEAs, and (c) platinum-FEAs, and (d) Ni FEAs, depending on radical treatment.

Table 1. Emission current fluctuations of amorphous carbon FEAs, TiN-FEAs, Pt-FEAs, and Ni FEAs with and without the radical treatment.

	Without radical treatment (%)	With radical treatment (%)
Amorphous carbon FEAs	±1.7	±5.1
TiN-FEAs	±2.5	±5.1
Pt-FEAs	±2.5	±8.1
Ni FEAs	±4.0	±10.1

However, the Ni FEAs were damaged and evaporated due to the arcing within 3 min, so that there was no pyramidal shape of FEAs. Fluctuations of Ni FEAs having no resistive layer increased from ±4.0% to ±10.0% concerning radical treatment in figure 6(d).

Moreover, in the case of our experiment system, the flux of oxygen radicals was 1×10^{15} atoms/cm^2·sec, 10^7–10^8 times higher than typical fluxes experienced by orbital satellites (about 10^7–10^8 atoms/cm^2·sec). The 30 minutes under in-situ oxygen radical treatment is equal to the corresponding time of the actual oxidation reaction for 0.3–3 years in LEO. Therefore, experimental

time of 30 minutes under in-situ oxygen radical treatment is quite enough to evaluate harsh environment characteristics.

Furthermore, amorphous carbon FEAs and TiN-FEAs, having a low work function as well as resistance to harsh environments, exhibit as stable fluctuations as ±5.1% even though FEAs were suffered by highly reactive oxygen radicals.

However, ±4% fluctuations for Ni FEAs increased ±10% in the condition of no resistive layer. Ni FEAs using a typical metal emitter material were destroyed and melted away. Work functions strongly influence the flicker noise concerning emission-current fluctuations [20]. It is regarded that work function at the surface of Ni FEAs is dependent on the adsorption (Ni–O) of active radicals such as O and the desorption processes. The work function increases due to adsorbates covering the Ni FEAs' surface so that current fluctuations, which closely depend on the work function, also increase. Therefore, amorphous carbon FEAs and TiN-FEAs with a low work function as well as resistance to highly oxidizing atmospheres exhibit comparatively stable field-emission characteristics. Especially, amorphous carbon FEAs exhibit more endurable field-emission characteristics than do FEAs coated with TiN because the amorphous carbon FEAs have the most uniform tip radii due to the lowest standard deviation of tip radii.

Nakamoto has come up with both of panel type and pixel type devices by using vacuum nanodevices for aerospace applications [3]. The electric propulsion system, e.g., hall thrusters, ion engines, pulse plasma thrusters (PPT), field-emission electric propulsion (FEEP) and EDTs, has good advantages in aerospace applications. Typical ion engines' designs such as are cylindrical structures; e.g., hollow-cathode for electron confinement and microwave discharge electrodes as waveguide tube. Those cylindrical structures cannot be fabricated on flat substrates, nor can their size or shape be modified.
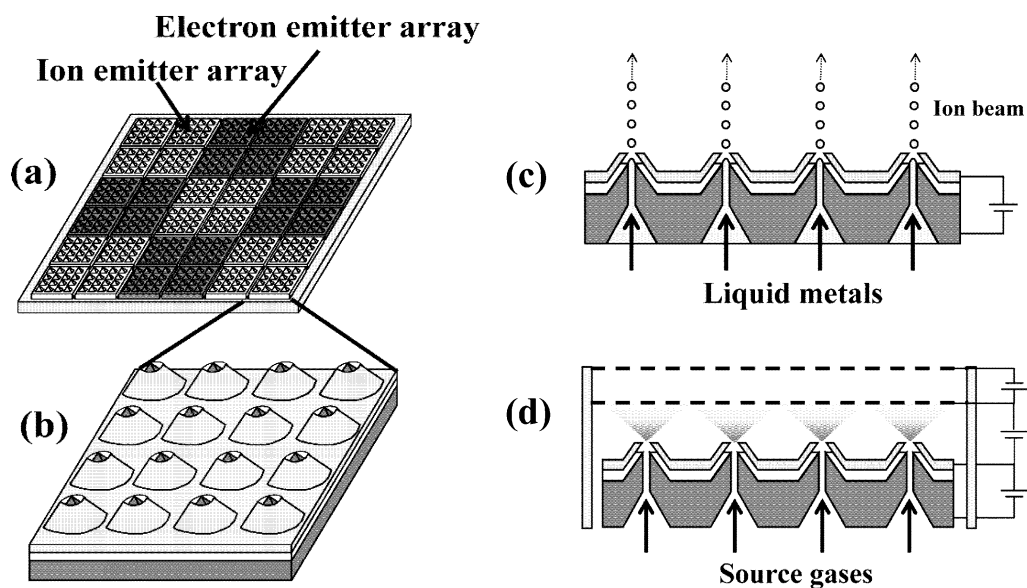
Figure 7. Proposed (a) panel-type and (b) pixel-type thrusters. Proposed schematic for thrusters using transfer mold FEAs for (c) field emission electric propulsion (FEEP) devices and (d) ion engines.

Figure 7 provides illustrations of ion-emitter arrays and electron-emitter arrays. Figures 7(a) and 7(b) show the proposed panel- and pixel-type electric thrusters, respectively. The (flat) panel type electric thrusters are assembled with nanoscale electron-emitter arrays, ion-emitter arrays and power supply units like an on-chip system. Electron-emitter arrays can compensate positive-charged ones as a neutralizer. Figures 7(c) and 7(d) exhibit the new pixel-type ion emitter arrays, which are made of either FEEP or ion engines having field emitter arrays. In the case of FEEP, electrons emit from FEAs so that metal cations are generated by alkali liquid metals such as Cs, which have a low ionization

potential (3.87 eV). In the ion engines, electrons emit from FEAs and are accelerated. Then, collisions between electrons and gas molecules in plasma can generate cations such as Xe^+ ions. The panel- and pixel-type electric thrusters can be assembled in a combination with electron emitters and ion emitters. Each electron and ion emitter is individually and digitally operated by variable numbers of emitters. Such a combination of pixel- and panel-type electric thrusters can be readily applicable to satellites regardless of their size.

4. Conclusion

Amorphous carbon FEAs produced by TMEFM can serve as remarkably stable vacuum nanodevices in highly oxidized atmospheres.

The evaluation results for field-emission stability were compared with those for TiN-, Pt-, and Ni-based FEAs. Amorphous carbon FEAs having no resistive layers had as low emission fluctuations as ±1.7%, which is one of the lowest ever reported. The amorphous carbon FEAs exhibit the most stable emissions, in comparison with emission fluctuations (±2.5%) of TiN-FEAs, because amorphous carbon FEAs have the most uniform tip radii. Also, FEAs fabricated by TMEFM exhibited both high environmental resistance and low work function as emitter materials, as well as possessed low fluctuations of about ±5.1% in highly oxidized atmospheres.

It is also recommended that the new ion engines and other aerospace devices that use the transfer mold FEAs should be assembled as combinations of pixel- and panel-type electric thrusters with ion-emitter arrays and electron-emitter arrays. Such combinations can be readily applicable to satellites of any size.

In summary, the remarkably uniform and low operation voltage amorphous carbon FEAs fabricated by the TMEFM show the most stable field-emission characteristics and the highest endurable field-emission characteristics in highly oxidized atmospheres. Thus, such FEAs are lucrative for making highly reliable and efficient electric thruster devices for satellites operating in various aggressive and highly oxidizing environments.

References

[1]   Nakamoto M and Fukuda K 2002 *Appl Surf Sci* **202** 289−94
[2]   Nakamoto M and Moon J 2011 *J Vac Sci Technol* B **29** 02B112-1−02B112-5
[3]   Nakamoto M, Moon J and Shiratori K 2010 *J Vac Sci Technol* B **28** C2B1−C2B5
[4]   Abe T, Knudsen D J, Yau A W, Watanabe S and Sagawa E 2001 *Adv Space Res* **27** 1403−12
[5]   Schafer J, Ristein J, Ley L 1997 *J Vac Sci Technol* A **15** 408−14
[6]   Robertson J 1992 *Phys Rev Lett* **68** 220−3
[7]   Joseph P T, Chen H C, Chen C H, Niu H, Tai N H and Lin I N 2011 *Mater Express* **1** 68−73
[8]   Lahiri I, Wong J, Zhou Z and Choi W 2012 *Appl Phys Lett* **101** 063110-1−063110-5
[9]   Nam J W, Alegaonkar P S, Park J H, Yoo J B, Choe D H, Kim J M and Kim W S 2007 *J Vac Sci Technol* B **25** 306−11
[10]   Spindt C A, Brodie I, Humphrey L and Westerberg E R 1976 *J Appl Phys* **47** 5248−62
[11]   Spindt C A, Holland C E, Schwoebel P R and Brodie I 1996 *J Vac Sci Technol* B **14** 1986−9
[12]   Itoh J, Tohma Y, Morikawa K, Kanemaru S and Shimizu K 1995 *J Vac Sci Technol* B **13** 1968−72
[13]   Lee N S, Chung D S, Han I T, Kang J H, Choi Y S, Kim H Y, Park S H, Jin Y W, Yi W K, Yun M J, Jung J E, Lee C J, You J H, Jo S H, Lee C G and Kim J M 2001 *Diam Relat Mater* **10** 265−70
[14]   Han I T, Kim H J, Park Y J, Lee N, Jang J E, Kim J W, Jung J E and Kim J M 2002 *Appl Phys Lett* **81** 2070−2
[15]   Pflug D G, Schattenburg M, Smith H I, Akinwande A I 2001 Tech Dig of the 47th IEEE IEDM, Washington, DC, USA, December 2–5, 2001, 179−82
[16]   Martin E E, Charbonnier F M, Dolan W, Dyke W P, Pitman H W and Trolan J K 1960 Technical Report of Wright Air Development Division **5**, 9−20

[17]   Charbonnier F M, Mackie W A, Hartman R L and Xie T 2001 J Vac Sci Technol B **19** 1064−72
[18]   Filik J, May P W, Pearce S R J, Wild R K, Hallam K R 2003 *Diam Relat Mater* **12** 974
[19]   Matsuo P J, Standaert T E, Allen S D, Oehrlein G S, Dalton T J 1999 *J Vac Sci Technol* B **17** 1435−47
[20]   Gotoh Y, Nagao M, Matsubara M, Inoue K, Tsui H and Ishikawa J 1996 *Jpn J Appl Phys* **35** L1297−L1300