**Supplementary Material**

**Fabrication, microstructure and enhanced thermionic electron emission properties of vertically aligned nitrogen-doped nanocrystalline diamond nanorods**

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***Figure S1.*** *(a) Bright-field TEM micrograph of U-DFs with corresponding SAED pattern as inset. (b) HRTEM micrograph, the structure image, of U-DFs, corresponding to the region “A” in “a”. The FT1FT3 images show the FT images corresponding to regions “13” of the structure image, respectively.*

The plan-view microstructure of the diamond films was analyzed using a transmission electron microscopy (TEM; JEOL-2100 operated at 200 kV). The bright field TEM micrograph in Fig. S1(a) reveals that the U-DFs contain very sharp grain boundaries of negligible thickness. Notably, in Fig. S1(a), only the grains oriented near some zone-axis strongly diffract electrons and show high contrast. The adjacent grains are oriented away from the zone-axis, showing no contrast. The discrete spot patterns in the SAED pattern [inset in Fig. S1(a)] indicates that the diamond grains in high contrast are oriented near the [011] zone axis, whereas the diffraction spots arranged along a ring, indicate that the background material contains other diamond grains that were randomly oriented. The HRTEM micrograph shown in Fig. S1(b) reveals the structure image of region ‘A’ in Fig. S1(a), indicating that the diamond grains contain a complicated microstructure. The FT diffractogram images (FT1−FT3) corresponding to the marked square regions “1−3” of Fig. S1(b) clearly gives evidence of polymorphs of diamonds and presence of stacking faults observed as the crisscrossed streaks in the images.

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***Figure S2.*** *(a) Plane view TEM micrograph of N-DFs with corresponding SAED pattern as inset. (b) HRTEM micrograph, the structure image, of N-DFs, corresponding to the region “A” in “a”. The ft1ft3 images show the FT images corresponding to regions “13” of the structure image, respectively.*

Figure S2(a) shows the plane-view TEM micrograph for the N-DFs with the inset showing the corresponding SAED pattern. The SAED contains sharp continuous diffraction rings corresponding to (111), (220) and (311) lattices planes of diamond that indicates the presence of randomly oriented small diamond grains. Some regions are of dark contrast, corresponding to diamond grains oriented along a zone-axis that diffracts electrons strongly, whereas some regions are of light contrast, corresponding to diamond grains oriented away from the zone-axis that diffract electrons weakly. A diffuse ring appears in the center of the SAED pattern, indicating the existence of a large proportion of *sp*2-bonded carbon (amorphous or crystalline). The HRTEM image, corresponding to region “A” in Fig. S2(a) is shown in Fig. S2(b). The diamond and *a*-*C* phases are highlighted by the Fourier transformed images. The FT1 image contains strong diffraction spots, which correspond to diamond (parallel fringes) in region “1”, and the FT2 and FT3 images corresponding to regions “2” and “3” correspond to *a*-*C* phases.

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***Figure S3.*** *(a) a AFM topographic scan (acquired during KPFM measurements) of the N-DNRs, (b) contact potential difference mapping and (c) the spatial variation of work function of the N-DNRs corresponding to “a”.*

For the evaluation of work function of the N-DNRs, a local probe-based electrical property measurements, KPFM measurements, were carried out as a non-contact local probe technique to map the work function of N-DNRs using a Au-coated Si tip with resonant frequency of 117 kHz. KPFM images were measured at normal atmosphere using two pass procedures, where the first pass with tapping mode atomic force microscopy (AFM) characterizes the topography and the second pass is accomplished with the probe lifted a set distance from the sample surface of the materials for mapping the contact potential difference (VCPD). During the second trace, the cantilever was not driven mechanically; instead, AC voltage of amplitude 2 V at resonance frequency was applied to the probe, and lift height was set to 25 nm. The work function of the N-DNRs was determined taking into account the value of the Au-coated Si tip work function, which is measured on a highly oriented pyrolytic graphite (HOPG) surface.

Notably, KPFM measurements is a non-contact AFM technique that affords topographic information and contact potential differences (VCPD) contrast of a sample surface with tens of millivolts of an energy resolution and a nanometer lateral resolution.[R1] The relationship between the VCPD and the work function (*ϕ*sample) of the sample can be expressed as, *φ*sample = *φ*tip – e (VCPD), where *φ*sample and the *ϕ*tip are the work functions of the sample and the tip of AFM, respectively, and e is the electronic charge.[R2] Figure S3(a) shows the topographic image of N-DNRs, whereas the corresponding VCPD mapping are shown in Fig. S3(b). The work function of the tips (Au-coated Si) was estimated with respect to HOPG and is found to be 4.73 eV. Accordingly, the average VCPD value obtained is ~0.098 V for the N-DNRs [Fig. S3(b)]. Based on the VCPD value and known tip work function for Au coated Si tip (4.73 eV), the value of work function for N-DNRs was estimated as ~4.65 eV for N-DNRs. The spatial variation of work function is shown in Fig. S3(c). These results show work functionvalue (4.5 eV) of N-DNRs calculated using R-D equation is close to the KPFM measured one. The small discrepancy in the values of work function obtained by KPFM with those derived from R-D equations is due to the difference in the electrical field (and temperature) applied in the two measurements. Moreover, the KPFM measurements were pursued at normal atmosphere and the absorption of gases from the environment could affect the KPFM measurements that increases the work function value. These results reveal that the fitting of the JTEE-T curves using the R-D model can provide the *ϕ*-value of the cathode materials with reasonable accuracy and, therefore, the R-D modelling on the JTEE-T curves can also provide a reasonable estimation on the Richardson constant, provided that the work function value used for modeling is accurate, viz. in good agreement with the *φ*-value measurement independently.

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***Figure S4.*** *Confocal micro-Raman (λ=488.0 nm) of I. U-DFs, II. U-DNRs, III. N-DFs and IV. N-DNRs.*

The bonding structure of the diamond materials were characterized using confocal micro-Raman spectroscopy (a Horiba Jobin-Yvon T64000 spectrometer with a laser source of 488.0 nm), respectively. Figure S4 shows the micro-Raman spectra of I. U-DFs, II. U-DNRs, III. N-DFs and IV. N-DNRs. The U-DFs (spectrum I of Fig. S4) comprise a sharp peak at the Raman shift of 1332 cm-1, representing the F2g-band of diamond (designated as “dia”) and a broad peak at 1486 cm cm-1 (G-band), representing the presence of graphitic carbon.[R3] The Raman spectrum of U-DNRs resemble the features of U-DFs. The RIE etching does not markedly influence the Raman characteristics of undoped diamond materials, except the induction of small Raman peak at 1380 cm-1 corresponding to disordered carbon due to RIE etching process. In contrast, the Raman spectrum of N-DFs (spectrum III of Fig. S4) contains Raman peaks, which are markedly broaden compared with those for U-DFs, inferring that the N-DFs contained markedly smaller diamond grains than the U-DFs. There are peaks at around 1140 cm-1 and 1520 cm-1, which are ascribed to the 1 and 3 modes of a *trans*-polyacetylene (*t*-PA) phase existing in the grain boundaries[R4] and the broadened peaks at around 1352 cm-1 (D-band) and 1560 cm-1 (G-band) correspond to disordered carbon and graphitic phases, respectively.[R5] Spectrum IV of N-DNRs shown in Fig. S4 shows that the “dia” and the G-band become slightly larger, entailing the improvement in crystallinity of both the nanodiamond grains and the nanographitic phases.[R6] A shoulder peak around 1600 cm−1 (designated as G´-band), which is not observed in the N-DFs (cf. spectrum III of Fig. S4), is seen that possibly arises from the presence of nanocrystalline graphitic in the N-DNRs.[R6] A reduction in the intensity of the *t*-PA peaks is observed for N-DNRs compared with those for N-DFs, which is an indication of the dissociation of C-H bonds in *t*-PA located at the grain boundaries of N-DNRs due to RIE process. These evolution of Raman characteristics is in accord with the proposed formation mechanism for the diamond nanorods for N-DNRs. That is, the species in the etching plasma preferentially interact with the grain boundary phases in RIE process. Moreover, it is to be noted that the sharp Raman peak at 1332 cm-1 corresponding to diamond is not evidently observed in the Raman spectra of N-DFs and N-DNRs (spectra III and IV of Fig. S4) because of the presence of nano-sized diamond grains in N-DFs (and N-DNRs). Moreover, the scattering cross-section for *sp*2-bonded carbon to incident laser in micro-Raman is markedly larger than that for *sp*3-bonded carbon that induced larger background noise in Raman spectra of these materials.[R6]

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***Figure S5.*** *C1s XPS spectra of I. U-DFs, II. U-DNRs, III. N-DFs and IV. N-DNRs.*

The surface composition and chemical states were investigated using XPS, which was performed using a Thermo-VG Scientific ESCALab 250 microprobe equipped with a monochromatic Al Kα X-ray source (1486.6 eV). The carbon 1s (C1s) core level peak of U-DFs(spectrum I of Fig. S5) is observed at 284.1 eV, which is attributed to bulk diamond (C-C).[R7] In contrast, the C1s peak of the U-DNRs (spectrum II of Fig. S5) blue-shifted to higher binding energy with respect to the U-DFs and shows a peak at 285.3 eV which is associated with *sp*3 C-C bonding in diamond. A contribution of *sp*2 C=C photoelectron component at 283.8 eV, which is associated with the reconstruction of diamond surface and bonding at grain boundaries due to RIE process.[R8] Moreover, the C=O peak is presented at 286.4 eV, which probably formed due to the interaction of O ions with the diamond during RIE etching. In contrast, the N-DFs contain a core level C1s peak at 285.0 eV (spectrum III of Fig. S5), which is associated with C-C bonding in diamond. There present C-N and C=N peaks located at 286.3, 287.3 eV, respectively.[R9] It should be mentioned that the C1speak of the N-DFs is observed at 285.0 eV, which is 0.9 eV higher compared to the C1speak of U-DFs (284.1 eV; spectrum I of Fig. S5). The cause of this difference in N-DFs is apparently due to the phenomenon that there present some CN species in the growing plasma (CH4/H2/N2) and the CN species have a stronger tendency to bind to the existing diamond clusters,[R10,R11] forming dangling bonds, which cannot be compensated effectively by the H- species. In contrast, the C1s peak for the N-DNRs consists of the *sp*3 C-C bonding peak at 285.3 eV and the *sp*2 C=C photoelectron component at ~284.8 eV (spectrum IV of Fig. S5), besides the presence of C-N /C=N peaks. Both C=C and C-C peaks of N-DNRs are broadened as compared to those for the N-DFs, which have been suggested due to the interactions of C with N species.[R12,R13] The broadened C=C and C-C peaks infer the induction of *sp*2-bonded carbon phases in N-DNRs because of the RIE process, effects that have also been demonstrated in the Raman spectra conversed earlier. Seemingly, a more abundant *sp*2 phases are present in the surface of the N-DNRs as compared to the other diamond samples that is an important factor, resulting in the enhancement of the TEE properties of N-DNRs.

**Table SI**. Comparison on the thermionic electron emission characteristics of refractory metals and nanocarbon thermionic emitters.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Materials | | *ϕ*  (eV) | Richardson constant  (A/cm2 K2) | JTEE  (A/cm2) |
| (a) | Molybdenum (Mo) [R14] | 4.15 | 3839 | - |
| Tungsten (W) [R15] | 4.54 | 55104 | - |
| Rhenium (Re)[R16] | 4.7 | 110320 | - |
| Cesium (Cs)[R17] | 1.81 | 162 | - |
| Cs/W[R18] | 1.36 | 3.2 | - |
| Molybdenum carbide[R19] | 3.7 | 23 | - |
| Tungsten carbide[R20] | 3.6 | 96 | - |
| Re+Carbide[R20] | 4.1 | 120 | - |
| N-DF/(N)UNCD/Mo [R21] | 1.42 | 0.69 | 200 A |
| N-DF/(N)UNCD/W [R21] | 1.38 | 1.69 | 500 A |
| N-DF/(N)UNCD/Mo-Re alloy[R21] | 1.4 | 3.67 | 1.4 mA |
| N-DF/(N)UNCD/Re(films)/Mo[R21] | 1.34 | 53.1 | 35 mA |
| (b) | MW-CNT yarns[R22] | 4.54 | 228 |  |
| Conical CNTs[R23] | 4.14.7 | --- | --- |
| P-doped dia./conical CNTs[R23] | 2.23 | --- | --- |
| undoped dia./conical CNTs[R23] | 4.26 | --- | --- |
| carbon nanofibers/Si wafer composites [R24] | 4.254.91 | --- |  |
| carbon nanofibers/carbon felt nanocomposites [R24] | 4.374.69 | --- |  |
| CVD grown graphene[R24] | 4.25–4.91 | --- |  |
|  | Graphene[R25] | 4.74.8 |  |  |

MW-CNTs: multiwalled-CNTs

UNCD: ultrananocrystalline diamond

**Table SII**. Comparison on the thermionic electron emission characteristics of N-DNRs with other diamond based thermionic emitters.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Materials | | *ϕ*  (eV) | Richardson constant  (A/cm2 K2) | JTEE  (A/cm2) |
| (a) | N-DF/N-UNCD[R26] | 1.29 | 0.8 | - |
| N-DF[R27] | 1.51.9 | 0.110 | 0.14 mA/cm2 |
| N-DF/Si [R28] | 1.99 | 70 | - |
| N-DF/Mo[R29] | 1.44 | 4.05 | 900 A/cm2 |
| N-DF/Mo(vac) [R29] | 1.30 | 1.0 | 3.0 mA |
| N-DF/Mo(CH4) [R29] | 1.43 | 10.7 | 5.0 |
| N-DF/Mo[R30] (H2 desorption) | 2.25 | 9.97 × 10-4 | 25 nA/cm2 |
| N-DF/Mo[R30] (H2 recovery) | 2.2 | 5.96 | 6 A/cm2 |
| (b) | S-doped diamond films[R31] | 1.9 | 1.0 | - |
| S-doped diamond/Mo films[R32] | 2.5 | 40 | 60cm |
| S-doped diamond/Mo films[R33] | 2.3 | 2.2 | 60cm |
| (c) | Heavily P-doped diamond films[R34] | 2.3 | 15 | - |
|  | P-doped diamond/Mo films[R35] | 0.9 | 10 A/cm2K2 | - |
| (d) | B-doped diamond/Mo[R36] | 4.43 | 60 | 0.8 nA |
| (e) | N-DNRsThis study | 4.5 | 18.0 | 12.0 mA/cm2 |

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