Electronic Supplementary Information (ESI)

Substrate-orientation dependent epitaxial growth of highly ordered diamond nanosheet arrays by chemical vapor deposition

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Figure S1 (a) SEM image of a HPHT diamond single crystal with {110}, {111}, {001}, and {113} facets used as the substrate for growing the DNSs. (b–h) Morphology of the DNSs arrays grown at the CH₄ concentration of 8.3% on different facets of the diamond single crystal for different growth time (temperature 1100 °C, pressure 25 kPa): (b) (110), 18 min; (c, d) (111), 26 min; (e, f) (001), 18 min; (g, h) (113), 26 min. Image d, f, and h were taken by rotating and tilting the sample holder to make 2 groups of the DNSs parallel to the electron beam.



Figure S2 Schematic illustration showing the geometrical relationship of the different groups of the DNSs on different planes of the diamond substrate. (a) (110). (b) (111). (c) (001). (d) (113).



Figure S3 SEM images of the DNSs grown on (111) plane substrates at different temperatures (CH₄ concentration 8.3%, pressure 25 kPa, growth time 26 min). (a) 1085 °C. (b) 1100 °C. (c) 1115 °C. (d) 1130 °C.



Figure S4 Lateral size vs. growth time (a) and thickness vs. CH₄ concentration (b) for the DNSs (growth conditions for curve a: CH₄ concentration 9.5%, 25 kPa; growth conditions for curve b: 25 kPa, 26 min).



Figure S5 SEM images of the DNSs grown on (110) plane substrates at different CH₄ concentrations (temperature 1100 °C, pressure 25 kPa, growth time 18 min). (a) 7%. (b) 9.5%.
(c) 11.7%. (d) 13.0%. (e) 15.3%. (f) 19.4%.



Figure S6 SEM images of the DNSs grown on (113) plane substrates at different CH₄ concentrations (temperature 1100 °C, pressure 25 kPa, growth time 18 min). (a) 7%. (b) 9.5%.
(c) 13%. (d) 16.3%. (e) 20.3%. (f) 22.2%.



Figure S7 SEM images of the DNSs on different crystal planes at different CH₄ concentrations (temperature 1100 °C, pressure 25 kPa, growth time 26 min). (a) (111), 7%. (b) (111), 15.3%. (c) (001), 7%. (d) (001), 15.3%.



Figure S8 Raman spectra of the diamond single crystal without growing the DNSs and the DNSs grown at different CH_4 concentrations (temperature 1100 °C, pressure 25 kPa, growth time 26 min).



Figure S9 DNSs on (110) diamond slices. (a) Optical photos of the diamond slices cut from HPHT single crystals before (A) and after growing the DNSs (B) and after etching in H_2SO_4/HNO_3 mixture (C). (b) Raman spectrum of the DNSs before and after etching. (c, d) SEM images of the DNSs arrays before (c) and after etching (d). The average thickness of the DNSs decreased from 30 to 23 nm after etching (growth conditions: temperature 1100 °C, CH₄ concentration 9.5%, pressure 25 kPa, time 26 min).



Figure S10 SEM images of the polycrystalline diamond films before (a) and after (b) growing the DNSs.



Figure S11 SEM images of the DNSs grown on {111} facets of polycrystalline diamond films under a bias of -60 V. (a) SEM image showing the triangle {111} facets. (b, c) Morphology of the DNSs arrays (Image c was taken by rotating and tilting the sample holder).
(d) Cross-sectional structure of the diamond/DNSs films.



Figure S12 SEM images of the DNSs arrays grown on $\{001\}$ facets under a bias of -60 V for 30 min (a, b) and 20 min (c). In panel a, the different structure of the DNSs on $\{111\}$ and $\{001\}$ facets can be observed. The images were taken by tilting the sample for 45° .



Figure S13 Cross-sectional SEM images of the diamond/DNSs films grown under a bias of -60V.



Figure S14 HRTEM image of a DNS (a) and the corresponding SAED pattern showing the twin structure (b). The SAED pattern shows two groups of diffraction spots with mirror relation, indicating that the DNS consists of the twin structure. (002)_G corresponds to graphitic layers.



Figure S15 TEM images of the DNSs without (a) and with graphitic overlayers (b, c) on the edge surface taken from the cross-sectional sample. In panel b, the DNS with graphitic layer on the edge surface is about 64 nm in height, which is much shorter than those with bare edge surface of 1.8 μ m in average height.



Figure S16 TEM images of the DNSs showing the epitaxial structure of the surface graphitic layers and inner diamond of the DNSs. (a) Low magnification image. (b) High magnification image taken from A area in panel a.



Figure S17 TEM images of a DNS with graphitic layer on the edge surface taken from the sample scraped from the substrates. (a) Overview image. (c, d) Edge structure.



Figure S18 Schematic illustration showing the epitaxial relationship between the graphitic layers and diamond. (a) Front view showing the lattice matching relationship. (b) Top view showing the registration relationship.