Nitrogen-incorporated ultrananocrystalline diamond and multi-layer-graphene-like hybrid carbon films

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Nitrogen-incorporated ultrananocrystalline diamond (N-UNCD) and multi-layer-graphene-like hybrid carbon films have been synthesized by microwave plasma enhanced chemical vapor deposition (MPECVD) on oxidized silicon which is pre-seeded with diamond nanoparticles. MPECVD of N-UNCD on nanodiamond seeds produces a base layer, from which carbon structures nucleate and grow perpendicularly to form standing carbon platelets. High-resolution transmission electron microscopy and Raman scattering measurements reveal that these carbon platelets are comprised of ultrananocrystalline diamond embedded in multilayer-graphene-like carbon structures. The hybrid carbon films are of low electrical resistivity. UNCD grains in the N-UNCD base layer and the hybrid carbon platelets serve as high-density diamond nuclei for the deposition of an electrically insulating UNCD film on it. Biocompatible carbon-based heaters made of low-resistivity hybrid carbon heaters encapsulated by insulating UNCD for possible electrosurgical applications have been demonstrated.

Carbon nanotube (CNT), carbon nanowalls (CNWs), graphene and multi-layer-graphene (MLG), nanodiamond (ND), and ultrananocrystalline diamond (UNCD) and their derivatives are among nanocarbons which have attracted profound scientific and technological interest because of their unique and excellent physical and chemical properties1–10. Three-dimensional and hybrid carbon films with outstanding properties such as standing multilayer-graphene-like carbon structures synthesized by plasma enhanced chemical vapor deposition (PECVD) on graphite and CVD diamond have been reported11,12. MLG has also been reported to grow hetero-epitaxially on nano-scale facets of (111) silicon13.

CNW is known to be made of stacked nano-graphite or nano-scale MLG with their basal planes being perpendicular to the substrate and has been synthesized by means of hot filament CVD (HF-CVD), catalytic CVD, radio-frequency (RF), direct-current (DC), and microwave plasma enhanced CVD (MPECVD) in hydrocarbon gas mixtures such as CH4 or C2H6 diluted by H211,14–19. Catalysts are not necessary for the synthesis of CNW, although in some cases, they are deliberately used. High-resolution transmission electron microscopy (HRTEM) reveals detailed microstructures of individual CNW to be of a decreasing thickness from the base to the top edge. Some CNW edges are ultra thin resembling nano-domain mono-layer or few-layer graphene20,21.

Although high-quality undoped UNCD is of high electrical resistivity, nitrogen-incorporated UNCD (N-UNCD) films deposited by MPECVD in Ar diluted CH4 with N2 additives have been shown to possess enlarged grain boundaries containing mainly sp2-bonded carbon species which significantly reduce the electrical resistivity of N-UNCD films22. Besides N-UNCD synthesized in Ar-diluted CH4, with N2 additives, MPECVD in H2-diluted CH4 with N2 additives has also been reported to synthesize N-UNCD. In the latter case, surface morphology of N-UNCD displaying sharp “ridge-like” microstructures was reported23. Although nitrogen is incorporated mainly in the grain boundaries of N-UNCD, nitrogen has been known to be a deep donor for diamond and also dope graphene and carbon nanowalls along with various kinds of defects in the graphene lattice structure24,25.

In this paper, low-resistivity nitrogen-incorporated hybrid carbon films exhibiting standing platelets carbon structures comprised of N-UNCD embedded between layers of MLG-like carbon films are reported. Unlike sharp “ridge-like” N-UNCD grown by MPECVD in H2-diluted CH4 with N2 additives, edges of hybrid carbon platelets become thicker when they grow taller. Scanning electron microscope (SEM), HR-TEM, and Raman spectroscopy
(RS), electrochemical etching, hydrogen plasma etching, heated oxidation in ambient air and electrical resistance measurements are applied to characterize the low-resistivity hybrid carbon films.

Diamond is chemically inert and biocompatible and, therefore, an excellent material for biomedical applications. Intrinsic diamond is an electrical insulator. When doped with impurities such as boron, diamond becomes a p-type semiconductor, of which the resistivity varies with the doping concentration from insulating to semi-metallic. The resistivity of lightly doped p-type diamond varies with temperature and can be used as a thermistor for measuring the diamond temperature. Boron-doped p-type microcrystalline CVD diamond deposited on an intrinsic CVD diamond film has been used to demonstrate biocompatible heaters\(^{26}\). Application of boron-doped microcrystalline CVD diamond heaters for catheter ablation in the heart was successfully demonstrated in cardiac muscle tissue of pigs\(^{27}\). For this application, lightly boron-doped CVD diamond served as thermistor for measuring the heater temperature. Unlike diamond, most resistive heater materials are neither chemically inert nor biocompatible. Biocompatible coatings, such as parylene, on resistive heating elements are, therefore, needed to protect the heating elements from direct contact and reactions with biomaterials\(^{28}\).

### Experimental

An MPECVD system (1.5 kW, 2.45 GHz, SEKI, Japan) is used for the synthesis of N-UNCD-MLG-like hybrid carbon films in Ar-diluted CH\(_4\) (1–3%) with N\(_2\) (1–50%) additives. Prior to the deposition, oxidized p-type (100) silicon substrates are immersed in a dimethyl sulfoxide (DMSO) solution containing detonation produced diamond nanoparticles which is under ultrasonic agitation for diamond nanoparticles to adhere on the substrate surface as diamond nuclei. Substrates are placed on a resistively heated molybdenum substrate holder. A thermocouple temperature sensor is inserted into the back side of the substrate holder for temperature measurements while a dual-color optical pyrometer is aimed at the substrate surface for non-contact measurement of the substrate temperature when the process plasma is turned off.

The substrate holder is preheated to 800 °C in vacuum by the resistive heater before MPECVD process begins. The surface temperature of the substrate measured by an optical pyrometer in vacuum is 50–100 °C lower than that of the substrate holder. During the deposition process, additional plasma heating and gas cooling result in the substrate temperature to become higher or lower than the 800 °C preheated substrate holder temperature. The measured temperature is 760, 860, and 890 °C for substrates after MPECVD processes in Ar-diluted 1, 2, and 3% CH\(_4\) with 20% N\(_2\) additive, respectively. The substrate temperature increases with CH\(_4\) content in the gas mixture. It indicates that heat flux to the substrate is higher for process plasma in a gas mixture with a higher percentage of CH\(_4\). Substrate temperature at around 800 °C is favorable for the growth of UNCD and MLG-like carbon species.

The reactor chamber is evacuated by a rotary vane pump to a base pressure of 8 mTorr. Process gases are fed through electronic mass flow controllers into the CVD chamber. The gas pressure is controlled by a throttle valve and a gas independent capacitive manometer. Unless otherwise stated, each MPECVD process is carried out in Ar-diluted 1, 2, or 3% CH\(_4\) with 20%–50% N\(_2\) additives at 90 Torr gas pressure under 1000 W applied microwave power for 1 hr. At the gas pressure of 90 Torr, frequent scattering by plasma species reduces the energy of ions bombarding the substrate.

A field emission SEM (JEOL JSM-7001) is used to observe the surface morphologies and cross-sectional images of the hybrid carbon films. HRTEM (JEOL 2100F) is applied to reveal microstructures of the carbon platelets. A three-electrode electrochemical system with a potentiostat (Autolab/PGSTAT302N) is used to selectively etch more reactive carbon species in the hybrid carbon films and expose N-UNCD by scanning the potential in a range exceeding the water splitting potential.

### Results and discussion

Fig. 1 shows SEM plan-view images and Raman (532 nm) spectra for carbon films deposited by MPECVD in Ar-diluted 1, 2, or 3% CH\(_4\) with 20% N\(_2\) additive at 90 Torr gas pressure under 1000 W applied microwave power for 1 hr. The surface morphology evolves from merged clusters of N-UNCD shown in Fig. 1(a) for 1% CH\(_4\) to bundles of line-shaped carbon structures shown in Fig. 1(e) for 3% CH\(_4\) with shorter line-shaped carbon structures appearing on the carbon film shown in Fig. 1(c) for 2% CH\(_4\).

Figs. 1(b), (d), and (f) show Raman spectra (532 nm) for the carbon films shown in Figs. 1(a), (c), and (e), respectively. The ratio of the Raman signal intensities, I(D)/I(G), of the D-band (1348, 1342, 1345 cm\(^{-1}\)) to that of the G-band (1552, 1580, and 1590 cm\(^{-1}\)) increases with the content of CH4 in the gas mixture and is measured to be 0.93, 1.2, and 1.4 for 1, 2, and 3% CH4, respectively. The I(D)/I(G) ratio is related to the crystallite sizes of the graphite grains or graphene domains in the carbon films\(^{29}\).

The Raman shift of the G-band from 1552 to 1590 cm\(^{-1}\) with increasing content of CH\(_4\) indicates an increasing content of graphene-like sp\(^2\) carbon in the carbon films besides N-UNCD. Before MLG-like carbon layers in the hybrid films grows to a significant size, the measured G-band is broad and overlaps with other Raman bands. MLG-like carbon layer in the carbon platelets causes the G-band to shift towards that of graphene at a higher wave-number. The synthesis of MLG-like carbon is further confirmed\(^{30–34}\) by the appearance of a narrower and stronger 2D-band near 2700 cm\(^{-1}\) shown in Fig. 1(f) than those in Figs. 1(b) and (d). Electrical conductivity of a hybrid carbon film increases with increasing CH\(_4\) in the MPECVD gas mixture due to increased contents of MLG-like carbon structures in the carbon film. In the following sections, hybrid carbon films deposited in Ar-diluted 3% CH\(_4\) with varied percentage of N\(_2\) additives will be based on for further discussion.

Fig. 2 shows TEM analysis of carbon films grown in a gas mixture of 20% N\(_2\), 3% CH\(_4\), and 77% Ar. Fig. 2(a) shows a TEM image of standing carbon platelets with the inset being a plan-view SEM image of the carbon film with standing platelet-like carbon structures. Amorphous carbon is deposited on the hybrid carbon film to fill the voids surrounded by standing carbon platelets. Dual-beam focused ion beam is applied to cut a slice of the hybrid carbon film.
in the direction parallel to the substrate for TEM analysis. The HRTEM images shown in Fig. 2(b) indicate that the standing carbon platelets contain N-UNCD sandwiched by or embedded in MLG-like carbon films. It is confirmed that the interlayer spacing for the inner N-UNCD is 0.224 nm corresponding to a diamond structure and the outer MLG-like carbon films have an interlayer spacing of 0.366 nm, which is close to that of graphite or MLG.

The electrical resistivity of hybrid carbon films decreases with increasing CH4 (from 1% to 3%) and N2 (from 1% to 50%) additives in which MPECVD is carried out. Surface enhanced Raman scattering of N-UNCD has shown that chain-like structures of sp2 and sp3 hybridized C and N assist ring clusters in the formation of a rigid connective network and that the grain boundaries exhibit characteristic bands of aromatic hydrocarbons and sp3 CH2 groups35,36. Graphitic carbon in the carbon films increases with the CH4 content in the gas mixture. Besides the low-resistivity of the N-UNCD base layer grown on the nanodiamond seeded substrate and the N-UNCD embedded inside the carbon platelets, MLG-like carbon films also contribute to the electrical conductivity of the hybrid carbon films. Sheet resistance of hybrid carbon films are measured between two metal contacts on two sides of rectangular shaped carbon films of known length and width. Fig. 3 shows the sheet resistance of hybrid carbon films with standing carbon platelets synthesized in Ar-diluted 3% CH4 with 20, 25, 30, 40, and 50% N2 additives. The sheet resistance is measured to be as low as 1.5 Ω/sq for hybrid carbon films synthesized in 50% N2, 3% CH4, and 47% Ar.

SEM images in Fig. 4 exhibit surface morphologies of three different areas on a hybrid carbon film. These images reveal that standing carbon structures grow from boundaries of N-UNCD clusters and then grow taller above the N-UNCD base layer. In Fig. 4(a), some carbon structures appearing differently from the merged clusters of N-UNCD in the N-UNCD base layer begin to grow and emerge from boundaries of N-UNCD clusters. These carbon structures grow at a high rate and perpendicularly to the N-UNCD base layer and evolve into standing carbon structures of different height shown in Fig. 4(c). Fig. 4(e) shows tall individual standing carbon structures. At this stage, the standing carbon structures appear similar to CNW.

Raman spectra shown in Figs. 4(b), (d), and (f), are measured from carbon films shown in Figs. 4(a), (c), and (e), respectively. When the standing carbon structures grow taller, the 2D-band signal intensity also increases, indicating that the MLG-like carbon contents in the standing carbon structures increases with growth time. In addition, the I(D)/I(G) ratio decreases with increasing 2D-band Raman signal intensity indicating that the Raman scattering signal is contributed by increasing amount of MLG-like carbon structures in the growing carbon film.

In order to reveal the contents of different carbon species in the hybrid carbon films synthesized in Ar-diluted 3% CH4 with 20% N2 additive, hydrogen plasma, electrochemical etching, and oxidation in air at elevated temperatures are applied to etch away more reactive carbon species. A Raman (532 nm) spectrum for the as-deposited carbon film shown in Fig. 5(a) is displayed in Fig. 5(b). Like MLG, the 2D-band Raman scattering signal intensity at 2702 cm⁻¹ is lower than that of the G-band27–31. As-deposited carbon platelets do not exhibit a diamond Raman peak because the resonant Raman scattering cross-sections for non-diamond carbon phases are much larger than that of diamond. When diamond is embedded between MLG-like carbon layers, the detectable diamond Raman signal intensity is too low to appear in a visible Raman spectrum (532 nm).
Atomic hydrogen react with both diamond and non-diamond carbon species to form hydrocarbons resulting in the etching of carbon species. Carbon platelets shown in Fig. 5(a) are exposed to microwave hydrogen plasma (1200 W, 40 Torr, 567 °C) for 1 hr. Carbon platelets after the exposure to the hydrogen plasma are shown by the SEM image in Fig. 5(c). The Raman spectrum shown in Fig. 5(d) exhibits a lower I(D)/I(G) ratio but a much stronger luminescence background for the hydrogen plasma etched carbon platelets than that of as-deposited one shown in Fig. 5(b). The strong luminescence is attributed to defects induced in the carbon film by ion bombardment and hydrogen etching. The signal intensity of the Raman band at 1140 cm⁻¹ originating from trans-poly-acetylene (TPA) is also decreased by plasma etching in hydrogen. It indicates that hydrogen plasma etches graphitic carbon species and TPA. Fig. 5(c) shows an SEM image of a hydrogen plasma etched carbon platelets. Carbon species which fill the space between carbon platelets are exposed because the tall carbon platelets have been etched and become shorter.

Fig. 5(e) shows the morphology of the carbon film after it is oxidized by the ambient air at 425 °C for 5 hrs. The surface morphology does not change as much as that after plasma etching in hydrogen shown in Fig. 5(c) from the as-deposited one shown in Fig. 5(a). Unlike hydrogen plasma etching, which etches both diamond and non-diamond carbon species and reduces the height of carbon platelets significantly, the surface morphology of the carbon film remains similar to the as-deposited one.

Fig. 5(f) shows a Raman spectrum of which both the D-band and the TPA-band signal intensities decrease significantly while that of the G-band increases, and that of the 2D-band remains similar after oxidation in air. The decrease in the I(D)/I(G) ratio is attributed to increasing average crystallite size of the MLG-like carbon films or the size of the nanographite grains because small sized ones are etched at higher rates by oxidation. Reactive carbon species, which contribute to the D-band signal intensity, are more easily etched by oxidation in air. Highly graphitized MLG-like carbon structures and N-UNCD in the carbon platelets are more resistive to oxidation in air.

Fig. 6 shows measured current from the first 50 cycles of cyclic voltammetric (CV) measurements of a hybrid carbon film in 0.1 M H₂SO₄ solution. The scan rate is 20 mV/s and the exposed electrode area is 0.071 cm². The as-deposited carbon film exhibits a small electrochemical potential window which is widened from cycle to cycle during its CV measurements. Reactive carbon species which cause high current in the CV measurements are gradually removed resulting in the carbon film surface being electrochemically stable carbon species such as N-UNCD. The current-voltage curve for the 50th cycle of the CV measurements is flat and of low current. The potential window becomes wider and wider towards that of a semiconductor diamond of nearly 4 V.

Electrochemical etching causes the surface morphology of the as-deposited carbon film shown in Fig. 1(e) to change to what is shown in Fig. 7(a). Fig. 7(a) exhibits clearer edges of carbon platelets and fewer carbon structures in the space between neighboring carbon platelets than the as-deposited carbon film. More reactive carbon species on the N-UNCD-MLG-like hybrid carbon platelets have been removed by the electrochemical process. UV Raman scattering (325 nm) further confirms the etching of non-diamond carbon species to expose N-UNCD by the higher signal intensity of the diamond UV Raman peak shown in Fig. 7(c) than that of as-deposited one shown Fig. 7(b).

UV Raman scattering is a non-resonant process for both diamond and non-diamond carbon species. Therefore, the Raman signal intensity is more proportional to the contents of diamond and non-diamond carbon species and diamond Raman signal is less likely to be covered up by much stronger signals from non-diamond carbon species. Besides the G-band (1593 cm⁻¹) and the D-band (1400 cm⁻¹), the spectrum shown in Fig. 7(b) for the as-grown carbon film displays a weak diamond Raman signal at 1334 cm⁻¹. After the carbon film is etched electrochemically, the Raman spectrum shown in Fig. 7(c) exhibits a diamond Raman peak of much higher signal intensity and at a lower wave-number of 1328 cm⁻¹. The increased signal intensity for the diamond Raman peak is attributed to the removal of non-diamond carbon species covering diamond grains in the carbon film. Selective etching of non-diamond carbon species in the hybrid carbon film changes the stress subjected to by diamond grains embedded in the carbon film and causes the diamond Raman peak to shift to a lower wave-number.

Standing carbon platelets comprised of N-UNCD which is sandwiched by or embedded in MLG-like carbon films exhibit increasing sheet resistance with decreasing N₂ additives. For a example, a hybrid carbon film deposited for 1 hr in Ar-diluted 3% CH₄ with 20% N₂ additive has a sheet resistance of 30 Ω/sq. The sheet resistance decreases further for higher CH₄ contents. For biocompatible applications in the environments of conductive liquids, the hybrid carbon heater must be encapsulated by an insulating biocompatible coating. By adjusting the CH₄ contents and the N₂ additives, resistance of a
hybrid carbon film can be optimized for specific applications such as electrosurgical heaters or electrically conductive probes.

Fig. 8 shows multi-layer carbon films needed for the fabrication of an UNCD encapsulated hybrid-carbon heater including an insulating UNCD base layer in Fig. 8(a), a low-resistivity hybrid carbon film deposited on the UNCD base layer in Fig. 8(b), and an insulating UNCD encapsulation layer deposited on the hybrid carbon film in Fig. 8(c). The electrically insulating UNCD film is deposited by MPECVD in Ar-diluted 1% CH4 without N2 additive at 700°C under 760 W microwave power for 1 hr. The hybrid carbon film is deposited by MPECVD in Ar-diluted 3% CH4 with 20% N2 additive at 850°C under 1000 W microwave power for 1 hr. Enhanced growth rate for the growth of hybrid carbon film grown on an UNCD film using the UNCD as diamond nuclei is shown by Fig. 8(b). The 5 μm thick hybrid carbon film shown in the upper part of the multi-layer carbon film in Fig. 8(b) is thicker than the 2.4 μm hybrid carbon film shown in the lower part of the multi-layer carbon film in Fig. 8(c) which deposited on nanodiamond seeded oxidized silicon. The 2.8 μm thick UNCD film shown by the upper part of Fig. 8(c), which is grown on top of a hybrid carbon film, is more than four times thicker than the 0.6 μm thick UNCD which is deposited on nanodiamond-seeded oxidized silicon as shown in Fig. 8(a). UNCD is an excellent substrate for the growth of the hybrid carbon film. The N-UNCD containing hybrid carbon film is also an excellent substrate for the growth of insulating UNCD. Without UNCD or N-UNCD containing hybrid carbon as a base layer, it takes extra nucleation and growth time for nanodiamond seeds to form a continuous carbon film and thus exhibits a lower growth rate for a fixed growth period of one hour.

Micro-Raman (532 nm and 325 nm) scattering is applied to analyze the insulating UNCD, the hybrid carbon film deposited on UNCD, and an insulating UNCD film deposited on the hybrid carbon film shown by the SEM images in Fig. 8. Fig. 9(a) exhibits Raman scattering (532 nm) signals characteristic of UNCD films such as the D-band at 1342 cm⁻¹, the G-band at 1540 cm⁻¹, and the TPA bands at 1140 and 1480 cm⁻¹. Raman spectrum excited by an UV laser (325 nm) for the UNCD film is shown in Fig. 9(b), which exhibits...
a diamond peak at 1331 cm$^{-1}$ besides the D-band at 1359 cm$^{-1}$, the G-band at 1572 cm$^{-1}$, and the TPA band at 1167 cm$^{-1}$. When the UNCD film is used as a substrate with embedded UNCD serving as diamond nuclei, the hybrid carbon film which is deposited on UNCD exhibits Raman spectra shown in Figs. 9(c) and (d) excited by 532 nm and 325 nm lasers, respectively. Besides the D-band at 1342 cm$^{-1}$, the G-band at 1595 cm$^{-1}$ and the TPA band at 1140 cm$^{-1}$, the Raman signal intensity for a 2-D band near 2684 cm$^{-1}$ is much stronger for the hybrid carbon film deposited on a UNCD in comparison with that for the UNCD film alone. The UV Raman spectrum in Fig. 9(d) shows that the hybrid carbon film deposited on the UNCD film exhibits a much weaker diamond Raman signal at 1333 cm$^{-1}$. The G-band shifts to 1590 cm$^{-1}$ and becomes narrower than what is shown in Fig. 9(b). It indicates that graphitic carbon in the hybrid carbon film is of larger crystallite sizes than that in UNCD. This is consistent with the existence of MLG-like carbon structures in the hybrid carbon platelets. When the hybrid carbon film is encapsulated by an insulating UNCD film, Figs. 9(e) and (f) show that both the visible (532 nm) and the UV (325 nm) Raman spectra for the top layer of UNCD are similar to those for the bottom layer of UNCD shown in Figs. 9(a) and (b).

Fig. 10(a) shows a flowchart for the fabrication of an UNCD encapsulated hybrid carbon heater and its measured temperature profile. N-UNCD in the hybrid carbon film, which is deposited on an insulating UNCD film, serves as diamond nuclei for the subsequent deposition of a low-resistivity hybrid carbon film. The hybrid carbon film is patterned by plasma assisted etching in oxygen using a molybdenum metal mask to remove unnecessary part of the hybrid carbon film and form a two-terminal resistor structure. The patterning can be either controlled by timing the etching process until the hybrid carbon is removed or allowing both the hybrid carbon film and the underlying UNCD to be etched away to form a C-shaped resistor. The metal mask is then etched to leave two metal contacts at two terminals of the resistor as well as needed interconnects with the remaining circuit. Fig. 10(b) shows a top-view schematic of the patterned hybrid carbon film heater deposited on an UNCD film with two metal contacts having been deposited on two terminals of the hybrid carbon heater. An electrically insulating UNCD film is then deposited in Ar-diluted 1% CH$_4$ without N$_2$ additive at 700°C under 760 W microwave power for 1 hr on top of the hybrid carbon film and the metal contacts and interconnects as an encapsulation layer. After both the hybrid carbon film and the underlying UNCD are etched, the subsequent deposition of the top layer UNCD also coats edges of the hybrid carbon resistor on the UNCD base layer. Therefore, the top layer UNCD and the UNCD base layer completely encapsulate the hybrid carbon resistor.

An applied voltage is across the two-terminals of the resistive heater. The surface temperature of the UNCD-encapsulated heater is measured by an optical thermometer. Red colored regions in the temperature profile shown in Fig. 10(c) represents the highest temperature measured on the surface of the heater. The temperature dependence on the resistance of the heater, the applied voltage, i.e., the extent of heating by the resistive heater, and the thermal conductivity of surrounding environments including the substrate. For the temperature profile shown in Fig. 10(c), an applied voltage of 5 V is applied between two contacts at two terminals labeled T1 and T2 with the highest measured temperature being about 50°C. UNCD encapsulated heaters are expected to be useful for biomedical applications. For example, some electrosurgical tools require low-voltage and biocompatible heaters. For treating cardiac arrhythmias, a resistive heater embedded in catheter can be used to ablate cardiac tissue. The biocompatible all-carbon resistive heater and the wear-resistant UNCD encapsulation layers are desirable for such an application.
Conclusions

Hybrid carbon films with standing carbon platelets grown on N-UNCD base layers are reported. The carbon platelets are comprised of N-UNCD which are sandwiched by or embedded in MLG-like carbon films. This multi-layer structure has been confirmed by means of HR-TEM and UV Raman scattering measurements. The novel hybrid carbon film is synthesized by MPE-CVD in Ar-diluted 3% CH₄ with 20–50% N₂ additive. The evolution of standing carbon structures to become hybrid carbon platelets are revealed by means of SEM. The hybrid carbon film is to some extent resistant to air oxidation at 425 °C. Repetitive CV measurements in H₂SO₄ solution cause preferential etching of reactive carbon species on the surface of the hybrid carbon film resulting in the widening of the electrochemical potential window towards that of semiconductor diamond of around 4 V. Low-resistivity hybrid carbon films are patterned to form resistive heaters. N-UNCD grains in the hybrid carbon films serve as high-density diamond nuclei for the subsequent deposition of pin-hole free insulating UNCD encapsulation layers for potential biocompatible applications of the UNCD encapsulated carbon-based heater.

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Author contributions

Y.T. wrote the main manuscript text, S.Y. and W.C.F. performed the materials synthesis and characterization, Y.C. contributed to the characterization and analysis of the data.

Additional information

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