Chemically induced transformation of chemical vapour deposition grown bilayer graphene into fluorinated single-layer diamond

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Notwithstanding the numerous density functional studies on the chemically induced transformation of multilayer graphene into a diamond-like film carried out to date, a comprehensive convincing experimental proof of such a conversion is still lacking. We show that the fluorination of graphene sheets in Bernal (AB)-stacked bilayer graphene grown by chemical vapour deposition on a single-crystal CuNi(111) surface triggers the formation of interlayer carbon–carbon bonds, resulting in a fluorinated diamond monolayer (‘F-diamane’). Induced by fluorine chemisorption, the phase transition from (AB)-stacked bilayer graphene to single-layer diamond was studied and verified by X-ray photoelectron spectroscopy, transmission electron microscopy and density functional theory calculations.

Graphene and diamond are two well-known carbon allotropes with sp2 and sp3 bonding hybridization, respectively, and are characterized by outstanding physical and chemical properties. Graphene is a single-atom-thick network of carbon atoms arranged in a hexagonal honeycomb lattice that has aroused a great deal of interest thanks to its high mechanical strength, high thermal and electrical conductivities, elasticity and so on. Diamond has an exceptionally high thermal conductivity, mechanical hardness and stiffness. A number of theoretical studies exist on the conversion of multilayer graphene into ultrathin ‘diamond’ films (these films are so thin, just a few layers thick, that they have been given a new name: diamane) by attaching fluorine or hydrogen atoms, or hydroxyl groups, to the outer surface of graphene films.

Two recent reports describe generating interlayer bonding between graphene layers but only during the application of very high pressure. Release of the pressure causes a return to the bilayer graphene (BLG), as described in both reports. One group reported the formation of an unstable interlayer bonded material (stable at high pressure only) in a diamond anvil cell as per changes in the Raman spectrum. The other group reported the local formation of interlayer bonding as a result of the high pressure applied by a silicone probe and a diamond indenter in an atomic force microscope; this region converted back to BLG when the high pressure was removed.

Our goal was to make diamane over a large area that was stable at ambient atmospheric pressure. Our strategy in our first attempts included noting that graphene functionalization with F atoms has several advantages over hydrogenation. First, according to the Pauling scale, the electronegativities of carbon, hydrogen and fluorine are 2.55, 2.20 and 3.98, respectively. Covalent C–F bonds are strongly polarized towards the F atom. Therefore, a fluorinated graphene structure can be quantitatively characterized using X-ray photoelectron spectroscopy (XPS) due to a strong binding energy shift of the C–F peak towards higher binding energies relative to the C–C (sp2/sp3) peaks in the Cls spectrum. Thus, XPS allows us to (accurately) characterize the configuration and the C/F stoichiometry of the fluorinated structure. In the case of hydrogenated graphene, it is impossible to quantitatively distinguish between C(sp2)–H and C(sp2)–C(sp3) bonds in the Cls XPS spectrum. In contrast with hydrogen, fluorine can be directly identified by XPS, energy dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS).

Second, common techniques of graphene hydrogenation or hydroxylation by ‘clean’ gas-phase reaction require the use of ‘hot’ hydrogen atoms or hydroxyl radicals that can be produced using hot filament,[6,9,12,13] high-pressure[5,8] or plasma[6,11,13] methods, which (at least at this early stage of diamane research) make it difficult to control the H/OH coverage and the stoichiometry as well as the degree of induced defects. Fluorination can be performed under moderate conditions (at near room temperatures and low/atmospheric pressure), for example by using xenon difluoride (XeF2) vapour as a source of fluorine.

Here we provide the first experimental evidence that carbon–carbon interlayer bonds are formed by the fluorination of BLG, and that this results in the formation of a thin film of fluorinated diamond (F-diamane). Our study used XPS, UV photoelectron spectroscopy (UPS), Raman spectroscopy, UV-Vis-NIR (near IR), EELS, transmission electron microscopy (TEM), scanning STEM (STEM) and density functional theory (DFT) to obtain structural information about F-diamane and to elucidate its formation mechanism.

To fluorinate graphene in a controllable and reproducible way, we used a home-built fluorination system that enabled us to control...
the partial pressure of the XeF₂ vapour and the temperature in the reaction chamber. By changing the fluorination conditions, such as temperature, XeF₂ partial pressure and exposure time, we were able to obtain fluorinated graphene structures having different C/F ratios. Next we provide a detailed description of our XPS studies that prove synthesis of F-diamane.

XPS was used to quantitatively characterize the fluorine coverage and to probe the nature of the chemical bonds of the graphene samples before and after fluorination. High-resolution core-level spectra and survey spectra were acquired for the as-grown graphene and for fluorinated films. Supplementary Fig. 1 shows the survey and core levels (C1s, Cu2p and Ni2p) of as-grown BLG on a single-crystal CuNi(111) alloy foil. The C1s spectrum of the BLG shows a single narrow asymmetric peak at 284.2 eV with a 0.58 eV full width at half maximum (FWHM), which is a signature of an sp²-hybridized carbon network. The high-resolution Cu2p and Ni2p spectra of the CuNi alloy substrate before fluorination correspond to metallic Cu and Ni (refs. 18,19).

Graphene films were fluorinated at 65 °C under 50–60 torr vapour pressure of XeF₂. Angle-resolved XPS (AR-XPS) was used to qualitatively study the distribution of chemical bonds over the layers by comparing relative intensities of the corresponding peaks obtained at 0° and 50° grazing emission angles between the surface normal and the direction towards the detector. Measurements taken at a 50° emission angle are more surface sensitive than those at 0° because of the difference in the photoelectron escape depth²⁰. After fluorination of the BLG on the CuNi(111) surface, XPS was used to quantitatively characterize the fluorine coverage and to qualitatively study the distribution of chemical bonds over the graphene layers by comparing relative intensities of the corresponding peaks to the C–F peak at 288.1 eV, which corresponds to 'bare' (not directly bonded to fluorine) carbon atoms adjacent to C–F groups and to C–F₂ or C–F₃ groups, respectively²²–²⁶. Strong shifts of these peaks (referred to as C–CF and C–CF₂,₃ in Fig. 1) to higher binding energies relative to C–C double bonds can be explained by the perturbation of the electronic structure of the bare C in the vicinity of covalent C–F and C–F₂ bonds due to the high electronegativity of fluorine. As Fig. 1 shows, prolonged fluorination (>12 h) of BLG on a single-crystal CuNi(111) surface under the conditions mentioned above results in the formation of the fluorinated structure, Sample A, with an essentially perfect C₂F₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆₁₈₁₈₂₆
By comparing the intensity ratios of the peak corresponding to \( sp^2 \) carbon (see Fig. 1) to the nearest peak (C–CF) associated with the presence of C–F bonds in the C1s spectra acquired at 0° and 50° emission angles (\( I_{50}/I_{C-C} \)), we can qualitatively analyse the distribution of C–F bonds over the layers. Thus, if the ratio, R, of \( I_{50}/I_{C-C} \) measured at 0° emission angle (\( I_{50}/I_{C-C}(0°) \)) to \( I_{50}/I_{C-C} \) obtained at 50° emission angle (\( I_{50}/I_{C-C}(50°) \)) is close to unity, this value indicates an even distribution of C–F covalent bonds over the layers; if \( R > 1 \), then the top layer of fluorinated BLG has a higher F content than the bottom layer, and if \( R < 1 \), then the top layer is less fluorinated than the bottom layer. According to the AR-XPS analysis shown in Fig. 1a–c, Sample A of an essentially C2F configuration has the ratio \( R = 1.14 \pm 0.05 \) and C \( (R = 1.37 \pm 0.05) \), the bottom layer has a lower fluorine content than the top layer. Also, in the binding energy range of 284–286 eV, Sample B has three distinct peaks while Samples A and C each have only two well-pronounced peaks in that range. The peaks at 284.9–285.3 eV are ascribed to the C–C \( sp^2 \) component and can be attributed to the formation of interlayer bonds. In the binding energy range 284.9–285.6 eV, two peaks, namely C–CF at 285.6 eV and C–C \( sp^2 \) at 284.9 eV, have been resolved for Sample B, whereas only one peak at 285.2–285.3 eV has been detected for Sample A and one peak at 285.5 eV has been observed for Sample C. We assume that the component at 284.9 eV in Sample B originates primarily from the carbon atoms in the bottom layer that have formed interlayer bonds with the carbon atoms in the top layer. Our assumption is based on the fact that since the bottom layer in Sample B is less fluorinated than the top layer, the C atoms in the bottom layer that form the interlayer bonds can generate a ‘pure’ \( sp^2 \) C–C signal at 284.9 eV, which is not strongly affected by the presence of carbon–fluorine bonds. At the same time, based on AR-XPS, the signals at 285.6 eV corresponding to the C–CF components in Samples B and C originate primarily from the top layer. By contrast, in Sample A, it is impossible to distinguish between the C–CF and C–C \( sp^2 \) components due to an essentially perfect CF stoichiometry and an even distribution of C–F bonds over the layers. Thus, every second C atom in Sample A, which may form an interlayer bond, is also adjacent to C atoms bonded to fluorine so that it is impossible to resolve ‘pure’ C–C \( sp^2 \) and C–CF signals. That explains the emergence of a single C–CF/\( sp^2 \) peak in the binding energy range 284.9–285.6 eV. In Sample C with a relatively low fluorine content (15–16 at.%), the signal corresponding to the C–C interlayer bonds has evidently not been detected because of a lack of C–F covalent bonds, which can stabilize the structure with interlayer linkages. A time-dependent XPS analysis of fluorinated Samples A, B and C was conducted and showed that the structures of Samples A and C are considerably more stable than the structure of Sample B (Supplementary Fig. 5).

The deconvolution of the F1s spectra (Supplementary Fig. 2) revealed signals corresponding to so-called semi-ionic/semi-covalent F–C bonds (686.7–686.9 eV)\textsuperscript{24–27}, ionic compounds (684.4–684.7 eV)\textsuperscript{21,22} and covalent F–C bonds (688.0–688.2 eV)\textsuperscript{23,24}. The AR-XPS showed that (1) the ionic signal is attributed to the fluorine bonded to metallic atoms, and (2) the F1s signal at 681.3–681.6 eV originates primarily not from the surface but from the graphene–metal interface or the interface between the graphene and the metal fluoride. These conclusions are based on the attenuation of the ionic and the physically adsorbed/entrapped peaks at the 50° emission angle relative to the main F–C component at 686.7–686.9 eV in the F1s spectra and relative to the C1s signal. The AR-XPS analyses of C1s and F1s spectra allow us to estimate the average thickness of the fluorinated BLG ‘over-layer’ (see Supplementary Table 2 for details). The fact that the signal at 681.3–681.6 eV is from the interface and not from fluorine intercalated between the graphene sheets has been tested in our analysis of fluorinated graphene film ’suspended’ on a TEM grid (as discussed below). The positions of the main C–F peaks at 686.7–686.9 eV and 287.9–288.2 eV in the F1s and C1s spectra, respectively, agree well with the corresponding values reported for semi-covalent/semi-ionic C–F bonds in fluorinated graphite/graphene structures\textsuperscript{24–27}. The covalent signal at 688.0–688.2 eV is assigned to C–F\textsubscript{3} bonds\textsuperscript{20}.

To characterize the nature of the C–F bonds in fluorinated BLGs, we analysed binding energy gaps between primary C–F peaks in the C1s and F1s spectra. Values ranging from 398.6 to 398.8 eV were obtained for all of our fluorinated BLG samples, consistent with covalent C–F bonding\textsuperscript{2}. The high binding energy satellite peaks in the Cu2p and Ni2p spectra, shown in Supplementary Fig. 6 indicate the formation of metal-fluoride compounds, CuF\textsubscript{2} and NiF\textsubscript{2}. This means that the graphene membrane is permeable to fluorine because of defects in the as-grown chemical vapour deposition (CVD) graphene and (perhaps also) its further damage during fluorination. The emergence of C–F\textsubscript{2}, C–F\textsubscript{3} and possibly C–O groups also confirms the presence of edges and defects in the graphene sheets.

The permeation of fluorine through the graphene membrane and further fluorination of the metal surface indicate the presence of fluorine at the BLG–metal interface that may lead to the fluorination of BLG from both sides, namely from the open surface of the top layer and from the bottom layer at the interface between the metal fluoride and graphene, and result in the formation of a double-layer of C\textsubscript{2}F stoichiometry stabilized with C–C interlayer linkages (Supplementary Fig. 2a), as suggested by the XPS results. The formation of the C\textsubscript{2}F configuration in Sample A (>12 h fluorination) through the intermediate states of Samples C (2–3 h fluorination) and B (5–6 h fluorination) suggests the mechanism of F-diamane formation on the metal surface, namely, the sequential fluorination of the top and bottom layers (top then bottom) in a relatively defective CVD-BLG. Defects in as-grown graphene may play a critical role in the emergence of the interlayer C–C bonds, which are nucleation sites, as a result of uneven fluorination of the BLG film, as shown by our XPS analysis of Samples B and C. In that case, F atoms at the interface form covalent bonds with the bottom layer to stabilize the local structure with interlayer C–C linkages, creating diamene nuclei. Further fluorination induces lateral propagation of C–C interlayer bonds, resulting in formation of the fluorinated diamond monolayer of an essentially perfect C\textsubscript{2}F stoichiometry (Sample A). No increase in the content of C–F covalent bonds was observed after fluorination for more than 12 h, confirming the complete conversion of BLG into an \( sp^3 \)-hybridized structure.

Supplementary Fig. 7 shows the calculated energies of pristine BLG with the unit cell containing 16 C atoms (C\textsubscript{16}) and of fluorinated BLG of different stoichiometries, namely C\textsubscript{16}F\textsubscript{3} with two F atoms on the top layer; C\textsubscript{16}F\textsubscript{3} with an interlayer C–C bond stabilized with two F atoms on the top layer and one F atom on the bottom (diamane nucleus); C\textsubscript{16}F\textsubscript{3} with a C–C interlayer linkage and two F atoms bonded to each layer; and C\textsubscript{16}F\textsubscript{3} (F-diamane). These configurations describe the evolution of BLG to F-diamane during fluorination. The fact that the energy of C\textsubscript{16}F\textsubscript{3} (with an interlayer C–C bond) is higher than the energy of C\textsubscript{16}F\textsubscript{3} (with no interlayer linkages) indicates the presence of a diamane nucleation barrier. If the barrier is high, the interlayer bond formation may start from a relatively defective CVD-BLG. A further increase in the fluorine content in the system (C\textsubscript{16}F\textsubscript{3} and \( x > 3 \)) induces the formation of more interlayer C–C bonds and leads to a decrease in energy. Once the bilayer structure ‘zips’ all the way through, the phase transition is complete, and highly stable F-diamane, as indicated by its very low energy, is formed.

The Raman spectra of as-grown BLG on the CuNi(111) surface, as well as the Raman signatures of Samples A, B and C, are shown.
in Fig. 2. The position, the FWHM, the shape of the 2D band and the ratio of the G to the 2D peak intensities obtained for the as-grown BLG transferred onto a SiO$_2$/Si wafer are typical of those of AB-stacked (Bernal) BLG (AB-BLG) (Supplementary Fig. 8). The Raman spectra of Sample C (15–16 at.% of fluorine) is shown in Fig. 2b. The emergence of a prominent D band at 1,360 cm$^{-1}$ indicates a strong modification of CVD-grown BLG on the CuNi(111) surface due to exposure to XeF$_2$. As fluorination time increased to ~6 h (Fig. 2c), the D peak increased in intensity and shifted below 1,350 cm$^{-1}$ while the 2D/G' graphene Raman decreased in intensity. In some regions in Sample B (25–27 at.% of fluorine), the Raman signatures were almost completely suppressed, indicating a high transparency of the fluorinated BLG structure. The Raman characterization of Sample A with 32–33 at.% of fluorine content showed a uniform structure over a large area with suppressed Raman signatures; this structure resembles that of fluorographene. In fluorographene, every carbon atom is covalently bound to a fluorine atom so that all carbon atoms are $sp^3$ hybridized. The dramatic change in Raman spectra of partially fluorinated BLG (though the fluorine contents in Samples A and B are close to each other: 32–33 at.% in Sample A vs 25–27 at.% in Sample B) can be rationalized by the fluorine chemisorption induced ‘zipping’ of highly fluorinated BLG, resulting in the formation of F-diamane (Sample A). Relatively weak D and G Raman signals in Sample A were observed in the isolated regions (domains) of a nearly hexagonal shape. Supplementary Fig. 9 shows Raman maps for as-grown BLG on CuNi(111) as well as for Samples A, B and C. Sample A showed the quenched Raman signal except for the domains with presumably trilayer graphene. We found hexagonal-shaped ABA-stacked trilayer graphene ‘patches’ in as-grown graphene film transferred onto a SiO$_2$/Si wafer (with a 300 nm thick SiO$_2$ surface layer) as shown in Supplementary Fig. 10. These isolated regions in Sample A can be distinguished under the optical microscope on the metal-fluoride surface (Supplementary Figs. 9 and 11) due to the difference in transparency of the continuous C$_3$F BLG (F-diamane) and the regions with presumably fluorinated ABA-stacked trilayer graphene domains (Supplementary Figs. 9 and 11). At the same time these regions are not visible either in the as-grown BLG on the CuNi(111) surface, or in Samples B and C with lower fluorine contents. ABA…-stacked multilayer graphene, including trilayer and thicker graphene films, cannot be converted into ‘thick’ diamanes because of the unfavourable Bernal (ABA…) layer stacking sequence, and thus the carbon atoms in every third layer are in the ‘wrong’ positions to form interlayer C–C linkages with the second layer. The layer stacking that would favour diamane formation for three or more layers is rhombohedral (ABC…). Hence, our optical microscope images and the Raman characterizations show the large area of ‘transparent’ regions in Sample A (of essentially C$_3$F stoichiometry), which indirectly proves the formation of a large area of F-diamane. The characteristic area of fluorinated monolayer diamond is constrained by the area of AB-BLG on the CuNi(111) surface.

UPS was carried out to characterize the valence band states in as-grown BLG as well as in fluorinated films with a different fluorine content (Samples A and B). The corresponding valence band

**Fig. 2** | Raman characterization of fluorinated BLG on the CuNi(111) surface. a–d. Raman spectra at six randomly chosen positions by 488 nm excitation of as-grown BLG (a), Sample C (2–3 h fluorination; b), Sample B (5–6 h fluorination; c) and Sample A (>12 h fluorination; d).
interatomic distances shown in Fig. 3b and in Supplementary structure on the CuNi(111) surface with characteristic interlayer/
ionization potentials of the fluorinated samples were calculated by -like density of states. After fluori-
(6.2) is attributed to the s-like density of states. After fluor-
nation, states emerged in the range 10–11.5 eV below the valence band maxima ascribed to the fluorine 2p-like states64. The UPS
srapameter of Sample A had two sharp peaks at 11.2 eV (fluorine 2p-like states) and 12.6 eV below the valence band maximum. The peak at 12.6 eV can be assigned to the diamond-like carbon 2s–2p hybridized orbitals9. The work function of pristine BLG and the ionization potentials of the fluorinated samples were calculated by subtracting the width of the photoelectron spectrum from the photon energy. Thus, the work function of as-grown BLG was found to be 4.4 eV. Ionization potentials of 6 eV and 8 eV were obtained for Samples A and B, respectively. The significant decrease in the spectral width after fluorination can be rationalized by the polar-
city of carbon–fluorine covalent bonds. The ionization potential of 8 eV measured for Sample A agrees well with the value of 8.71 eV estimated for F-diamane (for details see Supplementary Fig. 13). An ionization potential of ~8 eV was reported for the fluorine-ter-
minated diamond surface35.

TEM was used to explore the atomic arrangements in fluorii-
ated BLG on the single-crystal CuNi(111) surface. Experimental cross-sectional HR-TEM, STEM and simulated HR-TEM images are shown in Fig. 3 and Supplementary Fig. 14. The two-layer structure of the pristine graphene with a 3.24–3.41 Å interlayer separation was significantly altered upon exposure to XeF2. After fluorination, our TEM/STEM study revealed a highly ordered structure on the CuNi(111) surface with characteristic interlayer/interatomic distances shown in Fig. 3b and in Supplementary Fig. 14b. To elucidate the ordered arrangements of F and C atoms in the fluorinated BLG, simulated HR-TEM images were constructed for the DFT-optimized C2F configurations with and without interlayer linkages, as shown in Fig. 3c and in Supplementary Fig. 15. We note that our HR-TEM and STEM data give an average interlayer separation of about 2.05 Å (per the HR-TEM/STEM data, we fit between 1.93 and 2.18 in different regions). Note that the related d-spacing for diamond is 2.068 Å. Since neither an increase in interlayer spacing nor the characteristic atomic arrangements with F atoms alternately bound to each graphene layer from both sides were detected after fluorination, the emergence of the C2F configur-
ations without interlayer C–C bonds, including the most energeti-
cally favourable structure shown in Supplementary Fig. 15, can be ruled out. The simulated cross-sectional TEM images for the (110) and (100) planes of DFT-optimized F-diamane are given in Fig. 3c. It can be inferred from Fig. 3 and Supplementary Figs. 14b and 15 that the atomic arrangements and the interlayer/interatomic separa-
tions in the TEM/STEM images obtained after the fluorination of BLG on a CuNi(111) surface match well with those of the simulated F-diamane structure.

BLG fluorinated on a single-crystal CuNi(111) surface was then transferred onto gold TEM grids by using the electrochemical bubbling delamination method. We used two types of grids, namely, gold TEM grids covered with Quantifoil (2 μm hole size) and bare gold grids. The former, due to the good adhesion between graphene and a holey carbon support film, enables us to obtain a high-quality, large-area suspended BLG for HR-TEM, EELS, Raman spectroscopy and optical studies. The latter were used for the XPS character-
tization to determine the C/F ratio in suspended BLG without the ‘parasitic’ signal from the polymer support film.

To recover the fluorine content after the transfer process (Supplementary Fig. 16), the fluorinated BLG on the TEM grid was exposed to XeF2 vapour. According to the XPS and Raman analy-
(Fig. 4a,b), the C2F structure with quenched Raman graphene modes can be obtained after a 6 h fluorination of fluorinated BLG at 45 °C. A comparatively weak F1s ion signal detected in the sus-
pended sample is ascribed to the gold–fluoride compound, the for-
mation of which upon exposure of the gold TEM grid to XeF2 has also been verified by the emergence of prominent satellite peaks in the gold 4f high-resolution spectrum (Supplementary Fig. 17). The ratio, I(F)/I(A), of the integrated intensity of the F1s peak at 681.7 eV to the integrated intensity of the primary F–C peak at 686.7 eV in Fig. 4a (0.02) is one fifth of that obtained for a graphene film fluor-
inated on the metal surface (0.1). This result confirms that the primary source of the signal at 681.5 eV in the F1s spectra shown in Supplementary Fig. 2 is fluorine trapped between the bottom graph-
layer plane and the metal–fluoride surface.

UV-Vis-NIR absorption was measured for the films suspended on the gold TEM grid. The light beam was focused with a ×52 objective in order to sample an area of 1.5 μm–1.6 μm in diameter, thus within the holes in the carbon support film. Figure 4c shows representative absorption spectra of pristine and fluorinated BLG. The asymmetric absorption peak at 4.6 eV with ~6% absorption in the NIR range obtained for the pristine sample agrees well with the data reported for CVD-BLG61. For a fluorinated graphene film, significantly greater transparency in the visible range is attributed to the opening of a wide optical gap. According to the approach described in previous studies9,56 for 2D electronic systems, the optical gap can be estimated by using a linear approximation, as shown in Fig. 4c by the dashed line; the optical gap of fluorinated BLG was thus found to be in the range 3.3–3.4 eV. The experimental optical gap value of 3.3–3.4 eV is consistent with the calculated optical gap of 2.87 eV obtained for F-diamane (in comparison with the electronic band gap of 1.31 eV of the most energetically favourable C2F structure with no interlayer bonds). The calculated optical gap value of 2.87 eV was obtained by introducing an F monovacancy defect per 2 x 2 x 1 supercell (as shown in Supplementary Fig. 18); this monovacancy was found to induce a strong excitonic effect (see Supplementary information for details). The fact that the calculated value of the optical gap is lower than the experimental value can be rationalized by a relatively high concentration of F vacancies in our model of the ‘defective’ F-diamane, namely 12.5%, which cor-
responds to the C2F12 configuration.

Figure 5a,b shows the HR-TEM images and the selected area electron diffraction (SAED) patterns obtained for the fluorinated and non-fluorinated BLG, respectively. The number of layers in the graphene films was verified by in situ gradual, layer by layer, etch-
ing of the graphene sheets with an electron beam at an acceleration voltage of 80 kV (Supplementary Fig. 19)57. The SAED patterns were acquired from circular regions of ~0.7 μm diameter. The TEM data provided in Fig. 5 indicate a perfect in-plane hexagonal crystalline order in fluorinated and pristine BLGs. Detailed information on the atomic arrangements was gained by comparing the experimental TEM data with the simulated HR-TEM images of the DFT-optimized F-diamane (Fig. 5a), AB-BLG (Fig. 5b), C2F configuration without interlayer bonds (Supplementary Fig. 20a) and ABA-stacked trilayer graphene (Supplementary Fig. 20b). We examined the HR-TEM images by taking line profiles from the experimental and the simu-
lated micrographs, as indicated with the red and light blue lines and the corresponding insets in Fig. 5. In the micrographs of the fluori-
nated BLG and in the simulated TEM images of the DFT-optimized F-diamane, the contrast/brightness of individual dots is uniform. The corresponding line profiles measured for the fluorinated film are similar to those obtained for the simulated F-diamane. In con-
trast with the fluorinated film, in the pristine BLG case (Fig. 5b) six dots arranged in hexagonal rings appear to be brighter than the
Fig. 3 | TEM study of fluorinated BLG on the CuNi(111) surface. a,b, High-resolution cross-sectional transmission electron micrographs of as-grown (pristine) BLG (a) and Sample A (b). c, Simulated HR-TEM images of DFT-optimized F-diamane.

Fig. 4 | Spectroscopic analyses of fluorinated CVD BLG “suspended” on TEM grid. a, XPS C1s and F1s spectra of fluorinated BLG. b, Raman spectra of non-fluorinated/pristine BLG (BLG) and fluorinated BLG (F-BLG). c, Absorption spectra of BLG and F-BLG membranes.
dots located at the centre of these rings. We also analysed the intensity distribution over the diffraction peaks in the SAED patterns as well as in the digital diffractograms acquired for the DFT-optimized structures. For the obtained fluorinated film and the simulated F-diamane, the intensities of the first-order diffraction peaks are higher than those of the second-order peaks, with the experimental intensity ratio \( \frac{I_1}{I_2} \) values of 2.7–2.8. For both the BLG and the simulated AB-BLG, the first-order diffraction peaks have lower intensities than the second-order peaks \( \frac{I_1}{I_2} = 0.4–0.5 \), which indicates the AB (Bernal) stacking sequence in the double-layer graphene film. Hence, the micrographs and the diffraction patterns of the fluorinated and non-fluorinated BLGs are a good match to the corresponding simulated data obtained for F-diamane and AB-stacked BLG, respectively, as shown in Fig. 5. By decreasing the size of the parallel electron beam from 11.1 \( \mu \)m to 0.9 \( \mu \)m and hence by increasing the electron beam dose rate by more than 150 times, we observed the evolution of the SAED pattern of the fluorinated BLG from the characteristic diamane-like diffraction pattern to that of AB-BLG, as shown in Supplementary Fig. 21. The recovery of the AB-BLG structure is rationalized by defluorination of the graphene film, induced by an electron beam, as reported previously. Thus, electron beam irradiation of F-diamane can in the future be used as a nanopatterning technique to construct novel electronic devices by selectively restoring AB-BLG regions in an insulating ultrathin diamond-like structure. The SAED patterns collected at different locations across the fluorinated BLG film (each SAED pattern was acquired from circular region of ~0.7 \( \mu \)m diameter) indicate single crystallinity over a relatively large area (Supplementary Fig. 22).

F-diamane was further verified by TEM-EELS characterization. The K edge and low electron energy loss (EEL) spectra of the fluorinated and pristine AB-BLG are shown in Fig. 5c,d. The K edge spectral regions give important information about the bonding configuration \( sp^2/sp^3 \) in carbon materials and can be used for quantitative elemental/structural analysis while the low energy losses \(<100\text{eV}\) correspond to plasmons and interband excitations. In the pristine sample, the K edge spectrum of carbon atoms shows a clear \( sp^2 \) signal with sharp energy loss peaks at 285 eV \( (1s–2p(\pi^*)) \) and 292 eV \( (1s–2p(\sigma^*)) \). In the fluorinated BLG, the carbon K edge spectrum is dominated by \( 1s–2p(\sigma^*) \) features at 293 eV and 297 eV, whereas the \( 1s–2p(\pi^*) \) energy loss is strongly suppressed, indicating a lack of \( \pi^* \) orbitals. The disappearance of \( \pi^* \) anti-bonding states after fluorination of BLG was also confirmed by low EEL spectroscopy at energies below 60 eV. At the same time the C/F ratio estimated from the representative K edge spectral regions of carbon and fluorine (inset in Fig. 5c) is \( \sim 2.2 \) \( \left( C_2F_{3.9} \right) \), commensurate with the CxF stoichiometry identified by XPS. The main peak in the F K edge spectral region at 689 eV originates from the covalently bonded fluorine. Thus, the EELS data shown in Fig. 5c,d support

**Fig. 5** | TEM and EELS studies of fluorinated BLG membranes. a, b, TEM and EELS studies of fluorinated BLG. a, b, Experimental and simulated HR-TEM images and SAED patterns obtained for fluorinated BLG (a) and pristine AB-stacked (AB-BLG) (b). c, d, K edge and low EEL spectra measured for fluorinated BLG (F-BLG) (c) and non-fluorinated/pristine BLG (d).
the formation of a predominantly sp²-hybridized carbon structure (essentially, F-diamane with close to C,F stoichiometry) by the partial fluorination of AB-BLG. For comparison, in Fig. 5c we also provide the calculated K edge and low EEL spectra of F-diamane.

The results of the spectroscopic (XPS, Raman, UPS, UV-Vis, EELS) and microscopic (TEM, STEM) studies reported here indicate that fluorine chemisorption on CVD-grown BLG can result in a fluorinated diamond monolayer (F-diamane). F-diamane was obtained over a relatively large area, which is the area of as-grown AB-BLG on the CuNi(111) surface. F-diamane samples of (essentially) C,F configuration showed relatively high stability during the period when the data were being collected (∼48 h). The obtained diamond-like film is an ultra-thin semiconductor with a wide band gap, with electronic properties that are highly dependent on the surface termination species and which thus has potential for applications in nano-optics and nanoelectronics, and which can serve as a promising platform for micro- and nano-electromechanical systems. Also, F-diamane might have use as a seed layer for the growth of high-quality single-crystal diamond films by CVD methods under moderate conditions (pressure and temperature), or by other types of chemistry.

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**Methods**

**Preparation of CuNi alloys.** CuNi alloys were prepared by alloying single-crystal Cu(111) foils with Ni (∼20 at.% content) using electroplating and high-temperature (1,050 °C) annealing methods. Cu foil (20 μm, 99.9%, Nilaco) was heated at 1,050 °C with 10 s.c.c.m. Ar and 10 s.c.c.m. H₂ at atmospheric pressure (1 atm) for 12 h to convert it to a Cu(111) foil. Ni layers were then plated on the Cu(111) foil in an electrolytic solution, which was prepared by dissolving 140 g of NiSO₄·6H₂O, 4 g of NiCl₂·6H₂O, 2 g of NaF and 15 g of H₃BO₃ in 500 ml of deionized water. The current density in all the plating experiments was 0.02 A cm⁻². After washing and drying, the Ni-plated Cu(111) foils were placed in a quartz furnace and heated at 1,050 °C for 4–6 h in a gas flow of Ar (20 s.c.c.m.) and H₂ (20 s.c.c.m.) at atmospheric pressure.

**Synthesis of BLG films.** BLG was synthesized on single-crystal CuNi(111) by low-pressure CVD. Briefly, the low-pressure CVD was performed at 2.5 × 10⁻¹ torr and 1,075 °C by flowing an Ar/H₂ mixture (10/1 ratio) and CH₄(g) for 2 h through the CVD chamber. Details of the preparation procedure will be reported separately (M. Huang et al., accepted manuscript).

**Electrochemical bubbling delamination.** Graphene grown by CVD on the single-crystal CuNi(111) surface was spin-coated with a polymethyl methacrylate (PMMA) layer at 3,000 r.p.m. for 1 min to provide mechanical support for the transfer. The PMMA/graphene/CuNi(111) alloy foil stack was then dipped into a NaOH aqueous solution (1 M) to act as the cathode in an electrolysis cell with a constant current supply. The PMMA/graphene layer was detached from the CuNi(111) foil after tens of seconds as a result of the formation of a large number of hydrogen bubbles at the interface between the graphene and the CuNi(111) foil. After cleaning with deionized water, the floating PMMA/graphene layer was transferred to the target substrate (TEM grid or a SiO₂/Si wafer). Finally, the sample was dried and the PMMA was removed with acetone.

**X-ray photoemission spectroscopy.** High-resolution and survey spectra were acquired using the ESCALAB 250Xi XPS system with monochromatic Al Kα (E = 1,486.7 eV) X-rays and a 0.5 m Rowland circle monochromator. The ultimate system energy resolution was ∼0.40 eV. AR-XPS measurements were conducted by tilting a sample stage and hence by changing the electron emission angle from 0° to 56° between the surface normal and the direction towards the detector. High-resolution spectra were obtained at a pass energy of 20 eV. Alignment and calibration of the analyser was achieved using a standards block, which had samples of copper, silver and gold.

**Raman characterization.** Micro Raman measurements were conducted using a confocal Witec spectrometer with a 488 nm laser in the backscattering mode. A ×100 objective with a laser spot size of about 400 nm was used. To avoid significant heating and any other damage such as desorption of the adatoms from the graphene, the laser power was below 1 mW and the spectral resolution was ∼3 cm⁻¹.

**Transmission electron microscopy.** TEM, STEM and EELS characterizations were performed using an aberration-corrected Titan cube G2 operated at 80 kV. SAED patterns were acquired by using a ∼0.7 μm aperture. High-resolution TEM images were collected with a 0.2 s exposure time promptly after taking the SAED patterns to avoid significant electron beam damage (or defluorination), and images were filtered by the Wiener filtering method. EEL spectra were measured by a GIF Quantum ER system and the TEM-EELS method with an ~11 μm beam size, and a 5 mm entrance aperture was used to minimize beam damage (or defluorination).

Cross-sectional (S)TEM samples were prepared by a conventional focused ion beam technique using an FEI Helios Nanolab 450HP system.

**Optical characterization.** The absorption spectra of the graphene films were acquired using a CRAIC 20/20 PV UV-Vis-NIR microspectrophotometer. The measurements were conducted by focusing the light beam with a ×52 objective to sample an area of 1.5 μm–1.6 μm in diameter within the holes in the carbon support film.

**Data availability**
The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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**Author contributions**
R.S.R. and P.V.B. conceived of the experiment. P.V.B. wrote the manuscript; designed and constructed the experimental setup; and performed experiments, characterizations and data analyses. P.V.B. and R.S.R. revised the manuscript. M.H. prepared CuNi(111) alloys by electroplating and annealing synthesized and characterized graphene films on CuNi(111) alloy foils and performed the graphene transfer onto TEM grids and SiO₂/Si wafers; M.B. participated in making the metal alloy foils and synthesizing the graphene films. M.S. conducted the experiments and characterizations (transfer of the samples, assisting with building experimental setups and assisting with XPS and Raman characterizations). S.J. and Y.K. converted polycrystalline commercial Cu foils into single-crystal Cu(111). S.W.L. and Z.L. performed the TEM/STEM/EELS characterizations and TEM image simulations. S.H.J., S.O.P. and S.K.K. performed the DFT optimization and calculated formation energies as well as electronic and optical band gaps for various CₓF configurations (Supplementary Figs. 4, 13 and 18). J.D. and F.D. performed the DFT calculations to simulate the transformation of BLG into F-diamane (Supplementary Fig. 7), as well as performing EELS simulations. D.C.M. performed DFT calculations, electronic band structure calculations and the TEM/diffraction pattern image simulations.

**Competing interests**
The authors declare no competing interests.

**Additional information**
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