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DIAMANE AND DIAMANOIDS AS NEW NON-VDW 2D MATERIALS

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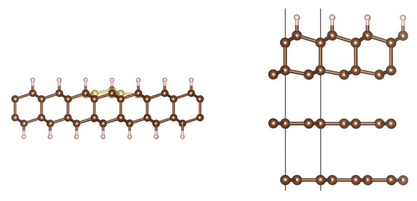
PURPOSE

To prepare diamane from the exposure of bi-layer graphene (2LG) to H radicals produced by the hot-filament process at low pressure and low temperature: sp^2-C to sp^3-C conversion is possible for AB and AA stacking, and is able to propagate across the layers in case of n(AAA) or n(ABC) stacking only.

To prepare diamanoid/graphene hybrids by replacing 2LG with few-layer graphene (FLG).

Diamane and diamanoids are promising new wide band-gap semiconducting materials for electronics, photonics and medical devices.

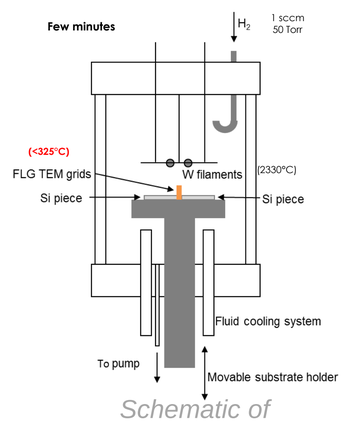


EXPERIMENTAL CONDITIONS

Starting materials
2LG
- As-received suspended 2LG graphene films grown by CVD and deposited on 3 mm ∅ Au Quantifoil TEM grid (commercialy available).
- Each film is polycrystalline; max. grain size of 20 μm. Grid coverage: ~98%.
- 2LG films were obtained from the successive transfer of two individual 1LG, hence the resulting 2LG stacking is random.
- Because of the grain size with respect to the film dimension, chances for locally getting the favorable AB or AA stacking configurations at micrometer scale are high.

FLG
- As-received suspended **FLG** films deposited on 3 mm ∅ TEM grids (*commercially available*).
- 1-6 layers; coverage: 60-90 %; grown on Ni and transferred using polymer-free method.
- The film is polycrystalline in the in-plane direction, but the layers within each grain are likely to be Bernal stacked or rotationally faulted.

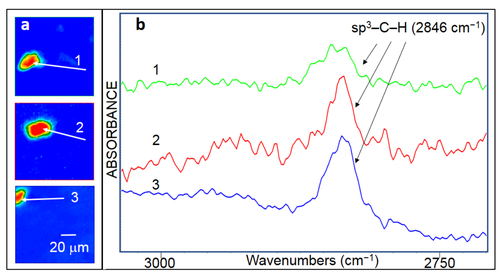
Hydrogenation process
- Hot-filament reactor ; 2 straight W wires; 2350 °C-2590 °C
- Gas: H_2 (99.999 % pure; 1 sccm; 50 Torr).
- Substrate max. temp: 400°C; Duration : 6'20".



Schematic of hydrogenation setup.

RESULTS

C-H BONDS

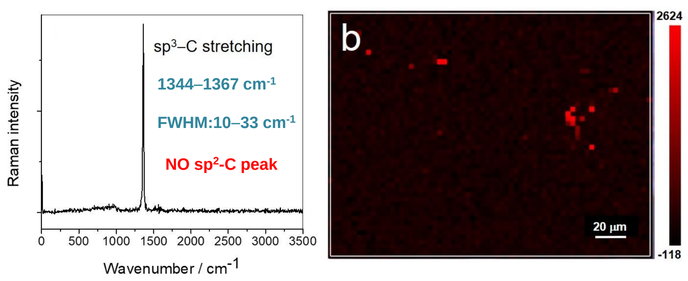


- **C-H bonds are formed.**
- **C bonded to only 1 H.**
- **Planes are hydrogenated, not only edges.**

(a) FTIR-ATR microscopy images processed on the integrated intensity of the associated C-C stretching band at ~1609 cm^{-1} that co-localizes with the C-H stretching band of FLG exposed to the hydrogenation process.
(b) Typical absorbance FTIR spectra (sums of 10 to 25 spectra per image) taken from pixels within the red regions arrowed in (a).

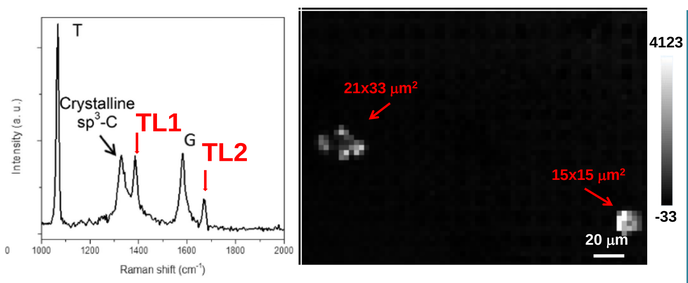
sp^2–C TO sp^3–C CONVERSION

DIAMANE



- Full conversion of 2LG into genuine diamane, can be obtained over 20 μm large region.
- Conversion takes place in regions where graphene sheets are AB- or AA-stacked.

DIAMANOIDS



- Partial conversion of FLG into diamanoid, can be obtained over 31 μm large region.
- Conversion takes place in regions where graphene sheets are AB-stacked.

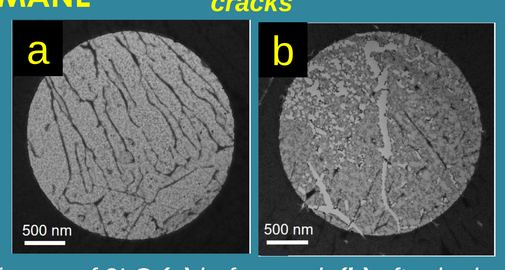
Raman spectra (@ 244 nm)

Raman map of the intensity of the sp^3–C stretching mode (diamond E_{2g} mode; lonsdaleite A_{1g} and E_{2g} modes).

STRESS

DIAMANE

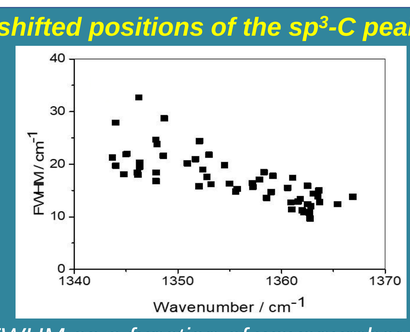
cracks



*TEM image of 2LG **(a)** before and **(b)** after hydrogenation.*

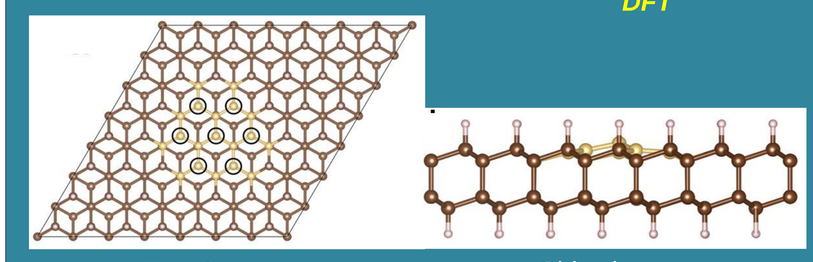
Stress ~ 10 GPa assuming an average hydrostatic strain

Up-shifted positions of the sp^3-C peak

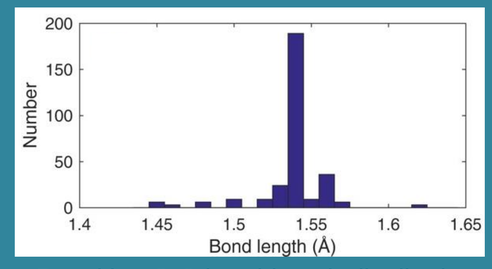


FWHM as a function of wavenumber of the sp^3–C stretching peak for 2LG exposed to the hydrogenation process.

DFT

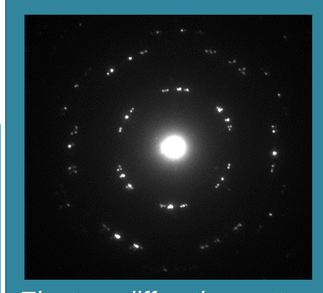


Reconstructed unsaturated structure, with 7 missing H on the top layer (position of the missing H atoms is given by the black circles)

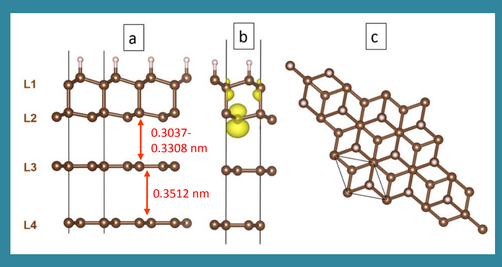


Resulting C-C bond-length distribution of the reconstructed unsaturated structure.

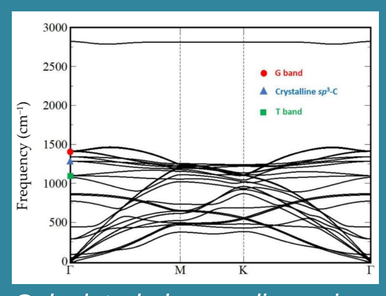
DIAMANOID


Electron diffraction pattern.

MODELLING



etc.
(a) and (b) two side view and (c) top view of the partially hydrogenated FLG used in DFT calculations with ABBA stacking.



Calculated phonon dispersion curve of the modeled system

- **T peak: combination of the stretching mode of the sp^3-C bonds with an optical out-of-plane mode (ZO) of graphene.**
- **"crystalline *sp*^{3}-C" peak : genuine *sp*^{3}-C layer between L_1 and L_2.**
- **G peak: unconverted graphenes such as L_4.**
- **TBL_1 and TBL_2 : bilayer configuration between L_3 and L_4 once twisted upon stress relaxation.**

High stress (33 GPa) is brought to L_4 and below → L_3 and L_4 in twisted-2LG configuration due to relaxation

CONCLUSION

- The hot-filament promoted hydrogenation process can be successfully used to produce genuine diamane from 2LG at low pressure and at low temperature.
- The key for producing homogenous diamane films is to start with very high quality 2LG material, ideally, single-crystal AB flakes as large as possible.
- If multi-domain 2LG containing a large proportion of randomly stacked layers and a lower proportion of AB and AA domains, are used, the hydrogenated material is under large stress (10 GPa).
- It is possible to produce diamanoid/twisted 2LG hybrids by using the same process by replacing 2LG by FLG.
- Twisted-2LG are presumably formed following the relaxation of the stress resulting from the partial sp^2-C to sp^3-C conversion, estimated at around 33 GPa by DFT calculations.
- sp^2-C to sp^3-C conversion is shown over surface areas of up to 2000 μm^2. It is believed that dimensions are only limited by the dimensions of the starting material, not by the process. Therefore, the results open the door to mass production of diamanes, diamanoids, and diamanoid/graphene hybrids (including twisted-2LG).

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