

## Supplementary information

### Nanoscale phenomena ruling deposition and intercalation of AlN at the graphene/SiC interface

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#### 1) Compositional analysis

Given the ultrathin nature of the intercalated structure with sub-layers of Al atoms at the graphene/SiC interface (and any other intercalated layers for that matter), compositional analysis by available methods is acknowledged as very challenging. Among the many aspects of consideration is the spatial selection/resolution, sensitivity to light/heavy atoms and signal-to-noise ratio. We have applied TEM based chemical analyses (EDS and EELS) to the intercalated structure with sub-layers of Al atoms at the graphene/SiC interface.

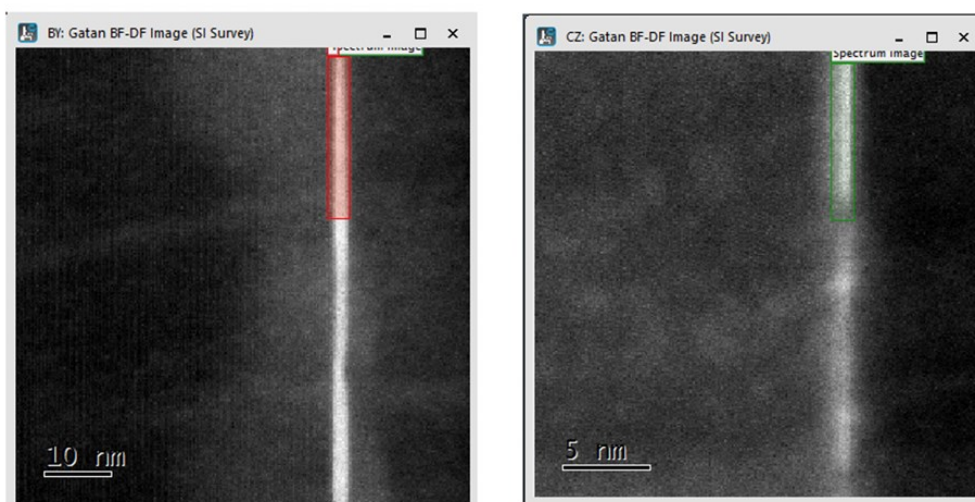
The EDS was acquired at 60 keV. On overall, it is easier to collect all the signals by EDS spectroscopy, but the detector itself is small compared to the whole solid angle which all the photons are emitted from, and it usually loses up to 70% of the emitted photons. **Figure S1** shows an EDS spectrum taken from the intercalated structure with sub-layers of Al atoms at the graphene/SiC interface. The position of the main elements within the intercalated structure is indicated, including Al K- $\alpha$  at 1.49 keV, and N K- $\alpha$  at 0.39 keV.

To increase the signal-to-noise ratio on the EELS acquired spectra, the electron dose was increased from 200 e-/Å<sup>2</sup> to 4000 e-/Å<sup>2</sup>. The increasing of the dose was found to cause damage to the intercalated layers and they eventually got destroyed after a single exposure (**Figure S2**, compare left to the right panel).

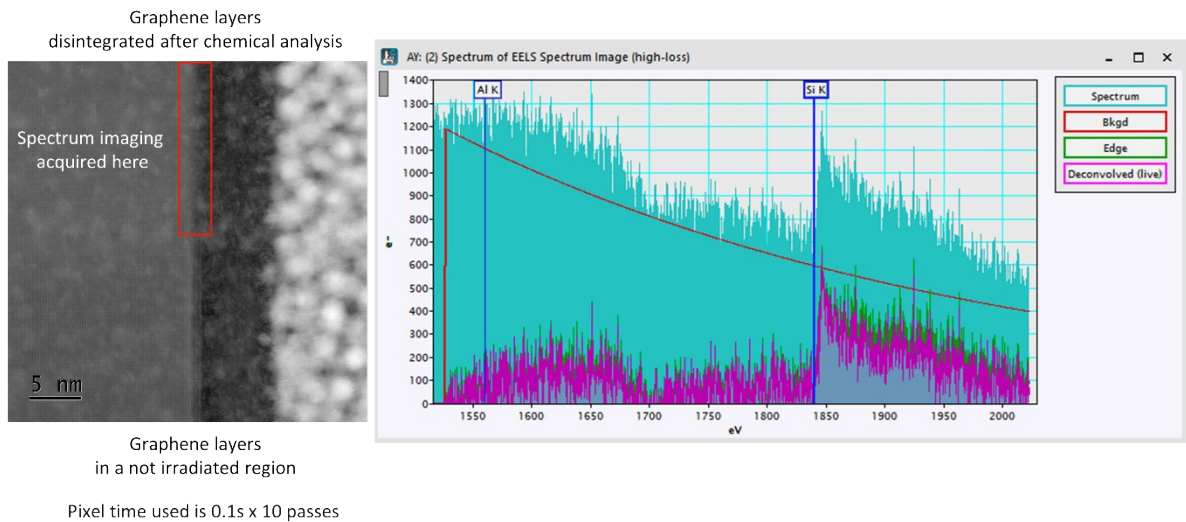
EELS spectrum from the intercalated structure with sub-layers of Al at the graphene/SiC interface was acquired at 200 keV (**Figure S3**). At very high energy loss the EELS cross section for electron-electron absorption is very low, thus, Al K-edge at 1560 eV from the ultrathin structure of two sub-layers of Al atoms intercalated at the graphene/SiC interface can mostly be observed as a small change in the noisy background slope. The Si K-edge at 1839 eV from the bulk SiC, since its much higher amount, is clearly visible instead.



**Figure S1.** EDS spectrum acquired from the intercalated structure with sub-layers of Al atoms at the graphene/SiC interface at 60 KeV of beam energy and 0.01 KeV of energy dispersion. The main elements C, N, O, Al, and Si are here labeled.



**Figure S2.** HAADF image of the intercalated structure with sub-layers of Al atoms at the graphene/SiC interface acquired at low (left) and high electron dose (right).

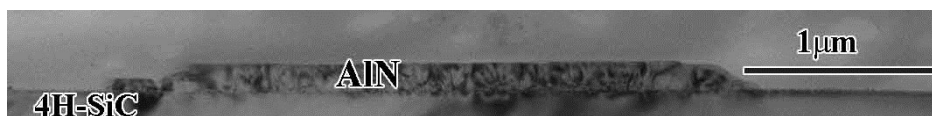


**Figure S3.** EELS spectrum from the intercalated structure with sub-layers of Al at the graphene/SiC interface. The extracted EELS spectrum (right image) results from the integration of the EELS spectra acquired over the interface within the area delimited by the red box present on the HAADF image (left image).

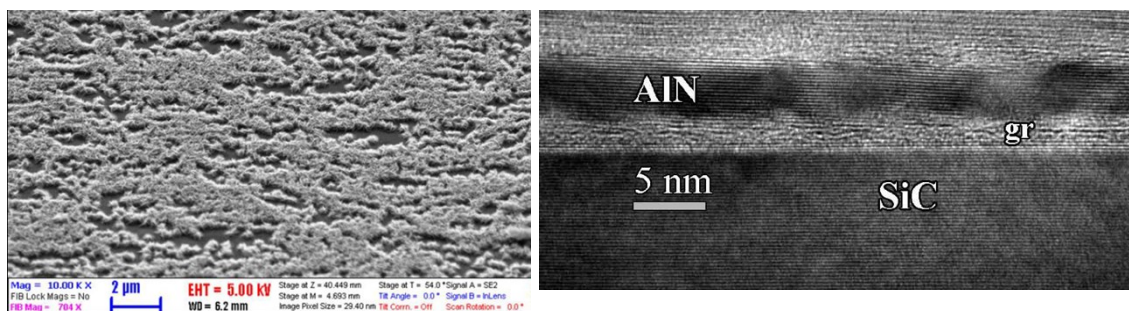
## 2) Notes on TEM

A low magnification TEM image of an AlN crystallite is shown in **Figure S4**. The TEM lamella was prepared from the sample representing the MOCVD of AlN on epitaxial graphene at the temperature of 1240°C. We note that, following the discussion in the main text, graphene could not be located at the AlN/SiC interface after the deposition at 1240°C.

Several TEM lamellas were prepared from the sample representing the MOCVD of AlN on epitaxial graphene at the temperature of 900°C after initial SEM observations (**Figure S5**).



**Figure S4.** Low magnification TEM image of an AlN crystallite following the MOCVD process at 1240°C.



**Figure S5.** (left) SEM image of the sample representing MOCVD of AlN on epitaxial graphene at the temperature of 900°C. It could be noticed that the sample exposes areas which are not covered by AlN. (right) HRTEM cross-sectional image of the same sample. This image shows a region where AlN over the partially damaged graphene is found by TEM. TEM is a high resolution, local method, which can trace the regions, where AlN is not nucleated on graphene (included in the main text) and other regions, where the nucleated AlN layer is thin (about 5 nm). We note that other regions yet, with thicker AlN have been represented by the corresponding AFM image in the main text.

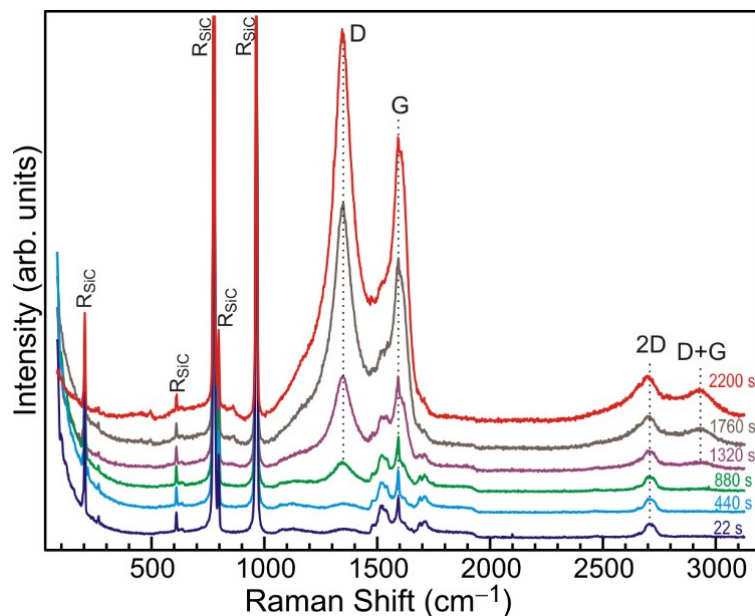
### 3) Notes on Raman spectroscopy

The characteristic  $E_2$  (high) phonon mode of 2D AlN is expected at  $659.9\text{ cm}^{-1}$ . However, its direct observation in Raman spectra using 532-nm laser excitation is deemed very difficult due to the following reasons: (i) the thickness of the material (two-layer) is very small, hence the volume excited by the laser is small and the expected signal is weak, (ii) the substrate exhibits rather strong second-order Raman bands in this spectral region, thus making the weak contribution from the 2D AlN indiscernible in the spectrum.

These restrictions can be alleviated to some extent by using UV excitation which will be absorbed in the top thin layer, thus bringing up its contribution and reducing the substrate contribution in the Raman spectrum. This approach has successfully been applied to 2D GaN, allowing for the registration of the phonon mode  $A_1(\text{LO})$ . [1]

However, the use of UV laser in the available range of lasers (350-364 nm) will amplify the contribution from the AlN and from the SiC substrate by approximately the same amount (proportional to  $1/\lambda^4$ , where  $\lambda$  is the laser wavelength), because it is not absorbed in the AlN layer owing to the much larger band gap than GaN. Weak contribution in the Raman spectrum from 2D AlN has been observed so far only on Si substrate which has relatively low Raman background contribution from the substrate in the region of  $660\text{ cm}^{-1}$ . [2]

From the theoretical modeling results, and as discussed in the manuscript, excess carbon species may be introduced to the structure because of the dissociative adsorption of the  $(\text{CH}_3)_3\text{Al}$  precursor, consequent to the  $(\text{CH}_3)_3\text{Al}/\text{graphene}$  surface reactions. Accumulation of amorphous carbon due to the dissociative adsorption of the  $(\text{CH}_3)_3\text{Al}$  precursor is indeed reflected in the intense and broad amorphous-carbon-resembling spectrum of the sample deposited at 700°C. Similar contribution is also expected in the sample deposited at 900°C. In fact, we have observed such contribution, but only after some annealing which occurs naturally in the laser spot during the Raman measurement despite the low laser power of  $< 1\text{ mW}$  (Figure S6).



**Figure S6.** Transformation of the Raman spectrum of the sample deposited at 900°C traced by recording one hundred spectra with 20 sec acquisition time per spectrum on the same spot on the sample. The changes in the spectrum are due to laser annealing of the sample at this spot. Only each 20-th spectrum is shown and each curve is labelled with the starting time of the acquisition with respect to the time of initial incidence of the laser on the sample. The intensity scale is the same for all spectra, but the curves are vertically displaced for convenient view. Note that the first ~20 spectra (represented by the two bottom curves) do not show any remarkable change, but after that the spectrum gradually develops towards "amorphous-carbon-like" spectrum. The prominent Raman peaks of the 4H-SiC substrate are labelled with  $R_{SiC}$ .

The exact annealing mechanism is not understood at present. The explanation of the observed effect may involve considerations about local (within the area of the laser spot) heat-driven aggregation of any remaining precursor-derived carbon species, albeit their total surface concentration is expected to be lower than in the 700°C sample due to increased volatility of these species at the higher temperature.

## References

- [1] Z. Y. Al Balushi, et al., *Nature Materials*, 2016, **15**, 1166; it is reference 12 from the main text of the manuscript.
- [2] W. Wang, et al., *Adv. Mater.*, 2019, **31**, 1803448; it is reference 11 from the main text of the manuscript.