Supporting Information

Direct observation of incommensurate-commensurate transition in graphene-hBN heterostructures via optical second harmonic generation

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Raman characterisation

We confirm the presence or absence of a commensurate phase at the interface between the crystals by Raman spectroscopy. Such an assumption is valid because of the commensurate phase for graphene on hBN is characterised by the appearance of a strain distribution when the crystals are near to alignment.[1] The Raman spectrum of graphene is sensitive to even slight changes in uniaxial/biaxial strain. In particular, it was shown that the 2D-peak responds to the commensurate phases' strain distribution by broadening.[2] Blue line in Fig. S2 shows that the full-width half-maximum of the 2D-peak (FWHM (2D)) before the phase transition is 23 cm^{-1}, which is consistent with an unaligned flake (>1.5° misalignment),[2] or graphene on a rough substrate (SiO_2, polymers etc.)[3] This observation indicates that the graphene and hBN crystals are not in the commensurate phase.

After the phase transition, the FWHM(2D) shows significant change. As shows the red line in Fig. S2, the width of the peak has broadened to 36 cm^{-1}, which is consistent with the most aligned case of graphene on hBN (0.3° alignment, moiré period is $L = 13.5$ nm). Corresponding results are shown in Fig. S1. Here, insets b and c depict the FWHM(2D) of two single-layer graphene flakes. The moiré period obtained for flake b is $L = 12.5$ nm (FWHM(2D) is 33 cm^{-1}).

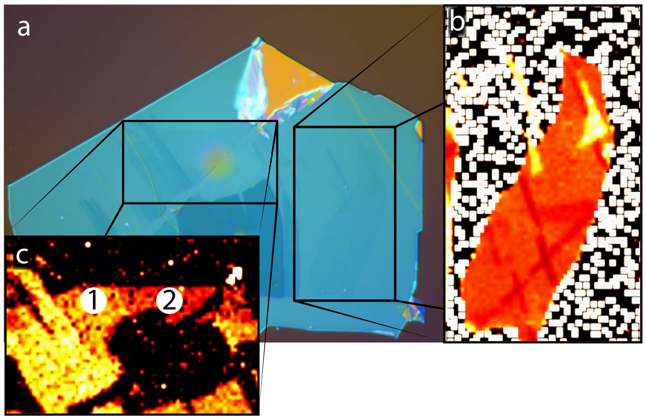

Figure S1: Optical image of the sample (a) and FWHM(2D) for single-layer graphene flakes (b and c) after the phase transition. Labels (1) and (2) on the panel c indicate regions with different moiré periodicity specified in the text.

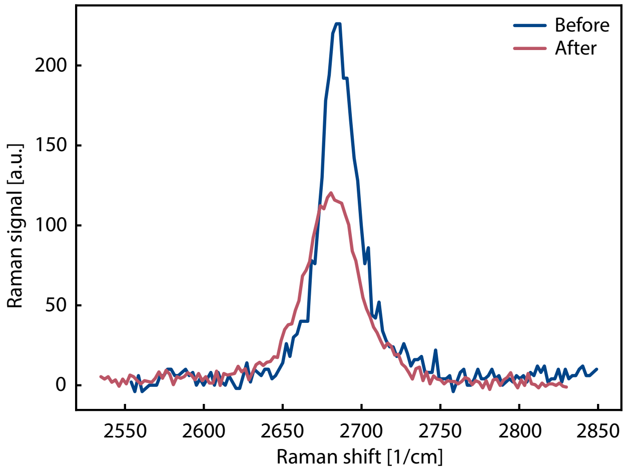

Figure S2: 2D-peak of the Raman spectrum before (blue line) and after (red line) the incommensurate-commensurate phase transition.

Moiré periods for areas (1) and (2) of the flake c are $L = 14.0$ nm (FWHM(2D) is 40 cm^{-1}) and $L = 12.5$ nm (FWHM(2D) is 33 cm^{-1}), respectively. This result demonstrates unambiguously that the graphene is now in a commensurate phase with the hBN crystal.

Encapsulated graphene

For additional confirmation of our findings, we repeat the nonlinear optical study on another sam-

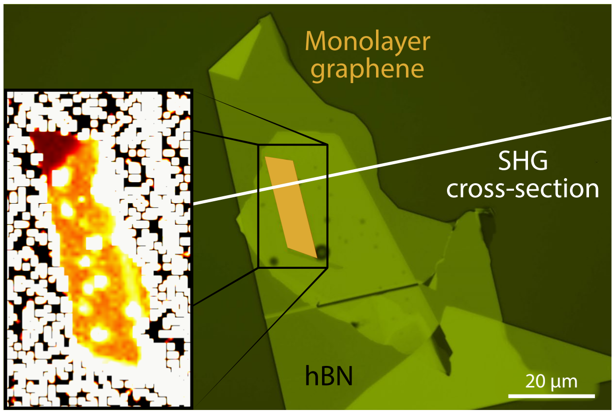

Figure S3: Optical image of the encapsulated and aligned graphene sample. A single-layer graphene flake is shown in yellow. The substrate hBN crystal is outlined in light green. Long white line indicates the cross section shown in Fig. S4 c. Scale bar is 20 um. The inset is a FWHM(2D) of the Raman spectrum.

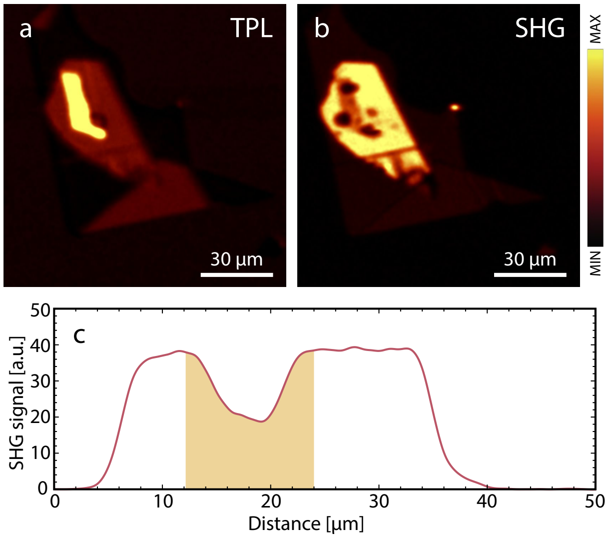

Figure S4: TPL (a) and SHG (b) signals from the aligned and encapsulated graphene/hBN heterostructure. Color bar depicts the intensity of the nonlinear response. A lighter color indicates a larger value of a signal. Panel (c) shows a cross-sections of the SHG signal depicted in Fig. S3. Yellow area highlights the reduction of the SHG signal due to a presence of the aligned graphene. The value of a signal is given in arbitrary units.

ple. The optical picture of the sample is shown in Fig. S3. Here, a yellow area highlights an aligned monolayer graphene encapsulated between two hBN layers depicted by a light green color. The alignment of the graphene is confirmed by Raman spectroscopy. The moiré period is found to be $L = 13.5\,\mathrm{nm}$ (FWHM(2D) is $37\,\mathrm{cm}^{-1}$).

The TPL and SHG intensity pictures are shown in Fig. S4 a and b, respectively. Here, both, the TPL and SHG responses clearly reveal the presence of a graphene flake. The change of the SHG signal from graphene with respect to the hBN environment confirms that the monolayer graphene flake is in the commensurate phase. The strong suppression of the SHG can be explicitly seen in Fig. S4 c that shows the cross-section of the SHG signal depicted by the white line in Fig. S3. Here, the yellow area corresponds to the position of the aligned single-layer graphene flake.

We also note that the SHG signal from the hBN area shown in Fig. S4 b is not uniform. The enhanced SHG signal that comes from both, upper and lower hBN layers, compared to the SHG response from only the lower one suggests that two hBN parts are not aligned with each other. This fact is also confirmed by a nonzero TPL signal from two-layer part of hBN shown in Fig. S4 a, meaning that the band gap of the double hBN is strongly reduced due to its incommensurate structure. As a consequence, the relative angles between graphene flake and lower and upper hBN layers are different. As we observe in Fig. S4 b, this results in a nonzero effect on the total SHG response from the encapsulated graphene area.

Finally, it should be mentioned that some defects are present in the Fig. S4 b. Dark round spots in the SHG image correspond to the areas that were burned during the signal optimisation process. For all presented samples, TPL had a higher absolute signal compared to the SHG. This means that a lower excitation power is needed to get an optimal signal for the TPL. The SHG signal is much more difficult to optimize, so a higher indent laser power wass used for a signal optimisation. TPL measurements were performed before SHG for a given sample, therefore the TPL image does not contain burned holes.

References

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