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Supplementary information of

Growth of High-quality GaN Crystal on BCN Nanosheet-coated Substrate by Hydride Vapor Phase Epitaxy

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1.1 Theoretical foundation

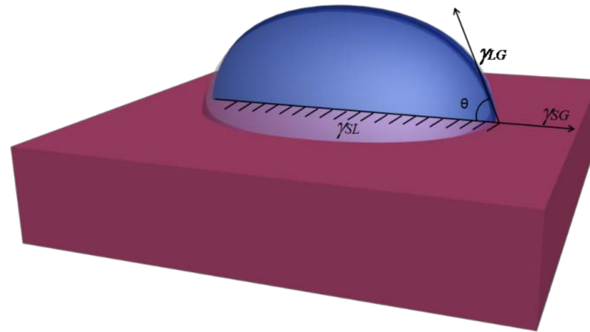

Fig.S1 Contact angle for a liquid droplet on a solid surface.

Wetting deals with the three phases of materials: gas, liquid and solid. The degree of wetting can be divided into four categories: perfectly non-wetting, low wettability, high wettability and perfect wetting. Only the high wettability needs to be considered for the wetting of BCN solution on MGA substrate.

Through simplification to planar geometry, Young relation, we can get that:[1]

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG}\cos\theta$$

where θ is the angle between the liquid and the solid phase, γ_{SG}, γ_{SL} and γ_{LG} represent the surface energy between the solid phase and the gas phase, the solid phase and the liquid phase, and the liquid phase and the gas phase, respectively.[2] Fig.S1 illustrates the contact angle of a liquid droplet wetted to a rigid solid surface, and Young relation can be deformed as:

$$\cos\theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}$$

1.2 AFM test results

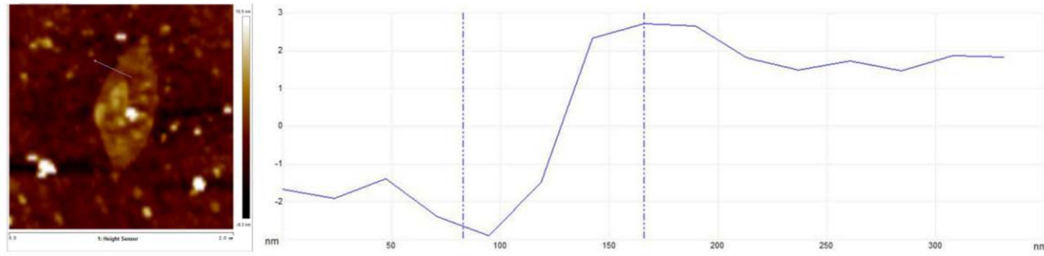

Fig.S2 AFM images of BCN nanosheets.

Fig.S2 shows the AFM images of the homemade BCN nanosheets by us. It is found that the BCN nanosheets are very thin and the thickness is about 5 nm

1.3 Formula Derivation

The nucleation rate *I* of crystals is expressed as:

$$I = Bn\exp[-\Delta G^* / kT] \quad 1$$

Where *B* is the probability of a crystal nucleus capturing a tour atom or molecule in a non-uniform nucleation, expressed as:

$$B = p(2\pi mkT)^{-1/2} \bullet \pi r^*{}_2 \quad 2$$

ΔG^* is the critical formation energy of the non-uniform nucleation, *k* is the Boltzmann constant, *T* is the Kelvin temperature, *m* is the mass of the atom or molecule, and r^* is the nucleation radius of the critical nucleation.

a). The critical formation energy ΔG_f^* derivation process on a flat substrate

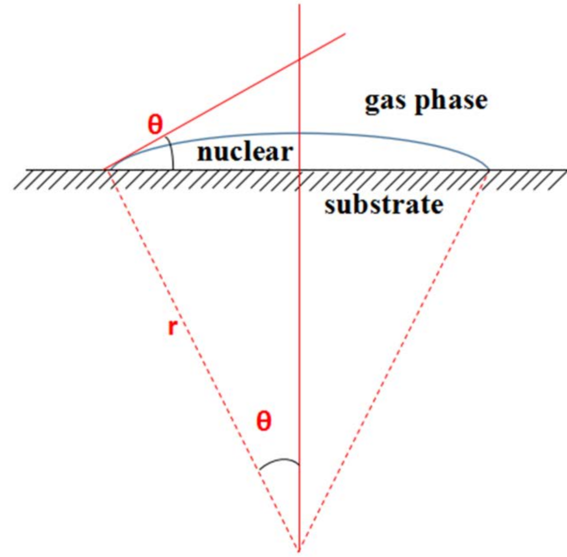

Fig.S3 Schematic diagram of spherical crown nucleation on a substrate.

Let $m=cos\ \theta$, then:

$$m = \cos\theta = \frac{\gamma_{sg} - \gamma_{sn}}{\gamma_{gn}} \quad 3$$

The crystal core volume V_n, the gas phase and the crystal core contact area A_{gn}, and the substrate and crystal core contact area A_{sn} are obtained:

$$V_n = \frac{\pi r^3}{3}(2+m)(1-m)^2 \quad 4$$

$$A_{gn} = 2\pi r^2(1-m) \quad 5$$

$$A_{sn} = \pi r^2(1-m^2) \quad 6$$

And ΔG_f can be calculated by the following formula:

$$\Delta G_f(r) = \frac{V_n}{\Omega_s}\Delta g + (A_{gn}\gamma_{gn} + A_{sn}\gamma_{sn} - A_{sn}\gamma_{sg}) \quad 7$$

Bring formula3, 4, 5 and 6 into formula7 to get:

$$\Delta G_f(r) = [\frac{4\pi r^3}{3\Omega_s}\Delta g + 4\pi r^2 \gamma_{gn}](2+m)(1-m)^2/4 \quad 8$$

Where Ω_s is the volume of a single atom and Δg is the phase change driving force.

Ind the derivative of r, and set $\frac{\partial G_f(r)}{\partial r} = 0$, we can get:

$$r_f* = \frac{2\gamma_{gn}\Omega_s}{\Delta g} \quad 9$$

Bring formula 9 into formula 8 to get:

$$\Delta G_f* = \frac{16\pi \Omega_s^2 \gamma_{gn}^3}{3\Delta g^2} \bullet f_1(m) \quad 10$$

Where f_1 is:

$$f_1(m) = (2+m)(1-m)^2/4 \quad 11$$

b). The derivation of critical formation energy ΔG_c* at concave corner

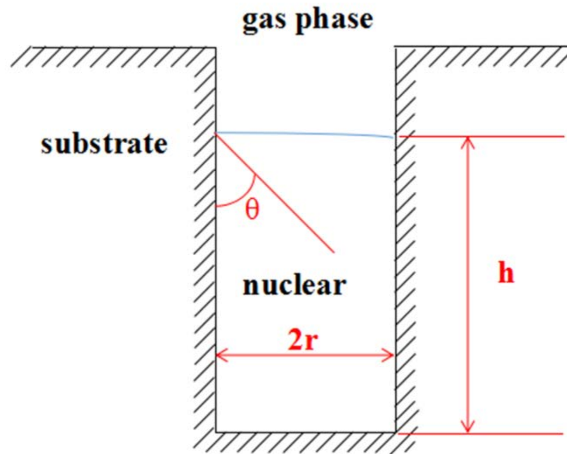

Fig.S4 Schematic diagram of concave angled core on the substrate.

Let $m=cos\ \theta$, then:

$$m = \cos\theta = \frac{\gamma_{sg} - \gamma_{sn}}{\gamma_{gn}} \qquad 3$$

The crystal core volume V_n, the gas phase and the crystal core contact area A_{gn}, and the substrate and crystal core contact area A_{sn} are obtained:

$$Vn = \pi r^2 h \qquad 12$$

$$A_{gn} = 2\pi r^2 (1 - \sqrt{1-m^2}) m^2 \qquad 13$$

$$A_{sn} = 2\pi r h + \pi r^2 \qquad 14$$

And ΔG_ccan be calculated by the following formula:

$$\Delta G_c(r) = \frac{V_n}{\Omega_s}\Delta g + (A_{gn}\gamma_{gn} + A_{sn}\gamma_{sn} - A_{sn}\gamma_{sg}) \qquad 15$$

Bring formula 3, 12, 13 and 14 into formula 15 to get:

$$\Delta G_c = \frac{\pi r^2 h}{\Omega_s}\Delta g + 2\pi r \gamma_{gn} \bullet [r(1-\sqrt{1-m^2})/m^2 - m(h+\frac{r}{2})] \qquad 16$$

Ind the derivative of r, and set $\frac{\partial G_f(r)}{\partial r} = 0$, we can get:

$$r_c{}^* = \frac{2\gamma_{gn}\Omega_s}{\Delta g} \qquad 17$$

Bring formula 17 into formula 16 to get:

$$\Delta G_c{}^* = \frac{16\pi \Omega_s{}^2 \gamma_{gn}{}^3}{3\Delta g^2} \bullet f_2(m) \qquad 18$$

Where f_2 is:

$$f_2(m) = \frac{1}{4}\{(\sqrt{1-m^2} - m) + \frac{2}{\pi}m^2(1-2m^2)^{1/2} + \frac{2}{\pi}m(1-m^2)\sin^{-1}(\frac{m^2}{1-m^2})^{1/2} - m(1-m^2) - \frac{2}{\pi r^*}\int_{mr^*}^{(1-m^2)^{1/2}r^*} \sin^{-1}[\frac{r^* m}{(r^* - y^2)^{1/2}}]dy\} \qquad 19$$

Finally, the formulas 2,10 and 19 are brought into the formula 1, which is available.

$$\ln(\frac{I_c}{I_f}) = \frac{16\pi\Omega_s^{\ 2}\gamma_{gn}^{\ 3}}{3\Delta g^2}(f_1(m) - f_2(m)) \qquad 20$$

And equation 20 is the ratio of the nucleation rate at the concave corner to the nucleation rate of the flat substrate.

1.4 PL test results

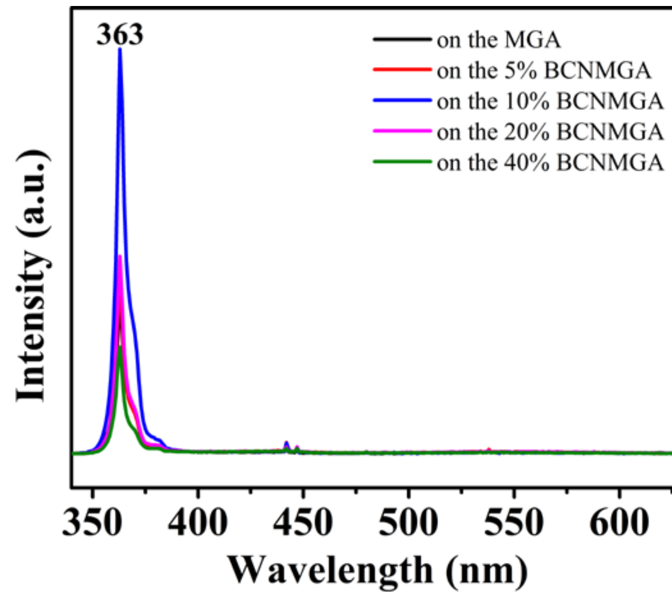

Fig.S4 PL spectra of the GaN crystals grown on the MGA and 5%, 10%, 20% and 40% BCNMGA templates.

From the PL spectrum, GaN grown on a common substrate also has a small peak around 360-380 nm, so the luminescence in the UV region has no relation with the introduction of BCN sheets. 360-380nm corresponds to 3.26-3.44eV, and the discussion is mainly referred to the following review.[3] The energy level corresponding

to 3.26eV is a shallow-level donor-acceptor pair (DAP) in the low temperature PL. With increasing temperature, the electrons from shallow donors thermalize to the conduction band, and the DAP transitions are gradually replaced by transitions from the conduction band to the same acceptor (e-A transitions). In this work PL measurements were carried out at room temperature (300K), so it can be considered that the peak mainly brought by the shallow level acceptor. It is reported in the literature that the introduction of Si is related to UVL, and C has no clear correlation. Si_N as a shallow acceptor is considered to be mainly caused by point defects in UVD in undoped GaN, and Mg_{Ga} is related to UVL in Mg-doped GaN. The growth of GaN in the manuscript is unintentional doping, so the influence of a quartz reactor or the like can be considered. The energy level corresponding to 3.44eV is called the two-electron satellite (TES) transition, which occurs when the excitons bound by the neutral donor (D^0X) are in the excited state and separated from the donor, and the TES is smaller than the corresponding D^0X. And the difference is the energy difference between the ground state and the excited state of D^0X. This transition is also considered to be related to the introduction of Si. In summary, the peak of the UV region in the PL spectrum has little to do with the C introduced by the BCN nanosheet, and this peak can also be confirmed by the fact that the GaN grown on the unprocessed substrate also has this peak. This peak is more closely related to the introduction of Si. Generally, undoped GaN samples exhibit certain unintentional doping n-type characteristics, which is consistent with other literature reports.

1.5 Substrate and as-obtained GaN single crystal

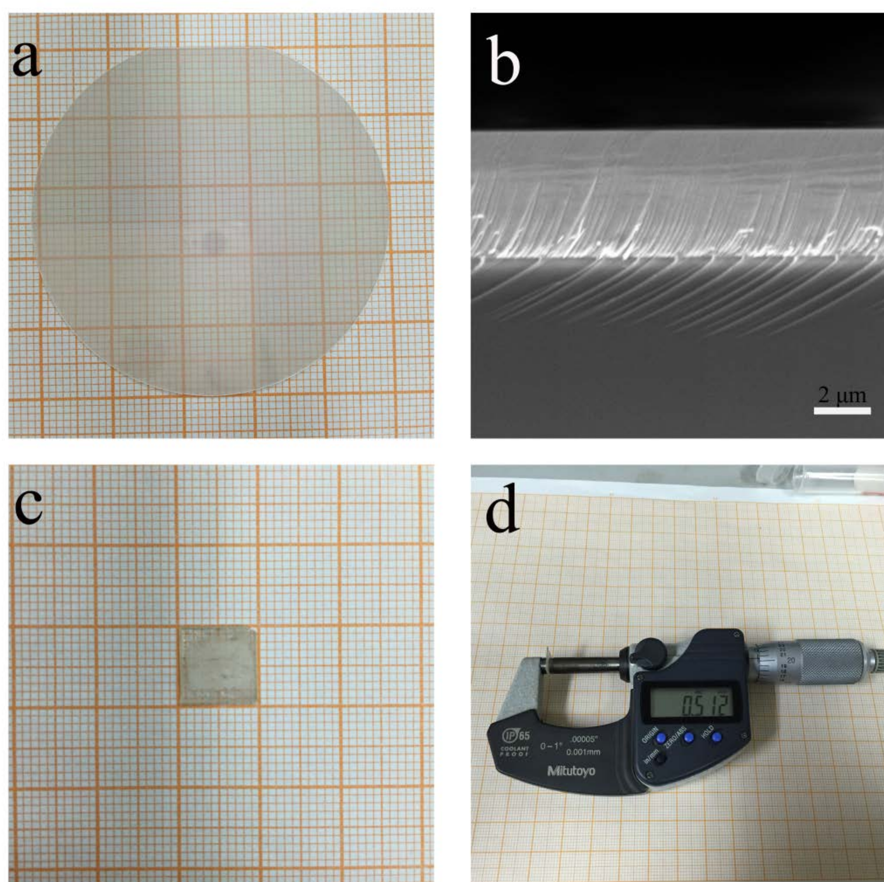

Fig.S5 (a) MOCVD-GaN/Al_2O_3 substrate, (b) cross-section SEM image of MOCVD-GaN/Al_2O_3 substrate; (c) GaN crystal grown on MOCVD-GaN/Al_2O_3 substrate coated with BCN nanosheets, and (d) thickness measurement result.

Fig.S5a shows a two-inch MOCVD-GaN/Al_2O_3 substrate, and Fig.S5b is the cross-sectional test surface of the substrate. The seed layer thickness is about 5μm. Fig.S5c is a GaN single crystal obtained after peel-cutting and its thickness is 512μm (Fig.S5d).

1.6 TEM test results

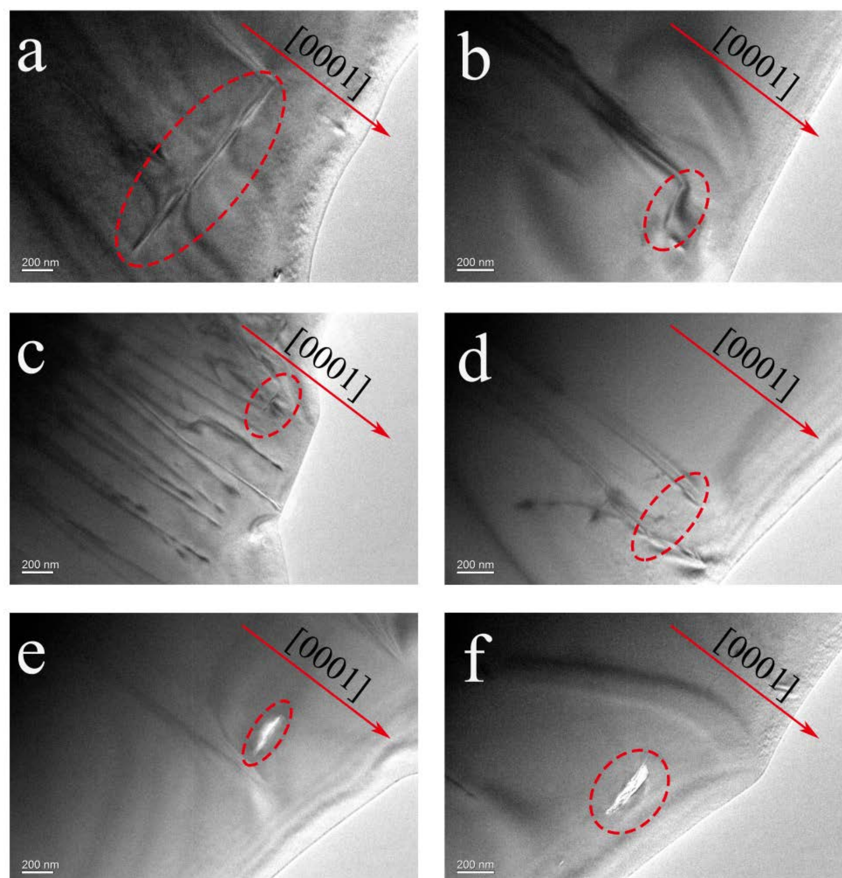

Fig.S6 TEM images of the GaN crystal grown on 10% BCNMGA template, the red circle is marked as a BCN nanosheet, and the black line in the test chart is the threading dislocation, and the red arrow direction is the [0001] direction, which is the direction in which the crystal growth direction is also the direction in which the dislocation extends.

It can be clearly seen from Fig.S6a, b, c and d that the extension of the local dislocations is terminated in the presence of BCN nanosheets, while in the absence of BCN nanosheets (Fig.S6c and d), the dislocations still extend along with the growth

of GaN crystal. And Fig.S6e and f show that BCN nanosheets do not introduce new threading dislocations, demonstrating that BCN nanosheets are suitable as coating materials.

References

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