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Supporting Information for

Subnanometer-thick 2D GaN film with large bandgap synthesized by plasma enhanced chemical vapor deposition

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Experimental section

Characterization

A Park NX10 AFM was applied to study the thickness and morphology of samples under non-contact mode. Thermo ESCALAB 250Xi XPS spectrometer equipped with a monochromatic Al Kα source was applied to obtain the chemical states. UV-vis absorption spectroscopy (Agilent Cary 60) was conducted on GaN film deposited on quartz plate. TEM (JEOL 2100F) with acceleration voltages of 200 kV was applied to characterize the crystalline structure of the samples.

Nitridation synthesis of 2D GaN film via PECVD

The as-prepared Ga_2O_3 film deposited on SiO_2/Si wafer was placed on a quartz boat in a sample film down position and further sent to the center of a quartz tube furnace. The system was heated up to 800 °C in 20 sccm Ar at a heating rate of 20 °C/min. Then 10 sccm N_2 was introduced to the chamber (initial pressure: 6 pa) with the microwave power set to 10 W. With the generation of nitrogen plasma, the chamber pressure slightly rose to 6.4 pa. The nitridation lasted for 2-60 min and then the system was cooled quickly to room temperature in 20 sccm Ar.

Fabrication of Ga_2O_3 film

As expected for a temperature-activated oxidation process, the Ga_2O_3 oxide thickness is studied to be increases with temperature [1]. It has been reported that low growth temperature (< 100 °C) result in oxide thickness below 4 nm [2]. Through a series of experiments, we found that 50 °C is an appropriate choice to fabricate uniform and thin Ga_2O_3 film as well as to facilitate the manual operations on the hot plate. In order to obtain the template film in a controlled manner, we studied the effect of the oxidation time on the thickness of the Ga_2O_3 film. During the squeeze-printing process, the liquid Ga droplet was left on the hotplate (under 50 °C) for 1 min and 5 min, respectively. As shown in Figure S2, the two Ga_2O_3 samples exhibit constant thickness, which is usually associated with the limiting oxide thickness achieved under low temperature [3].

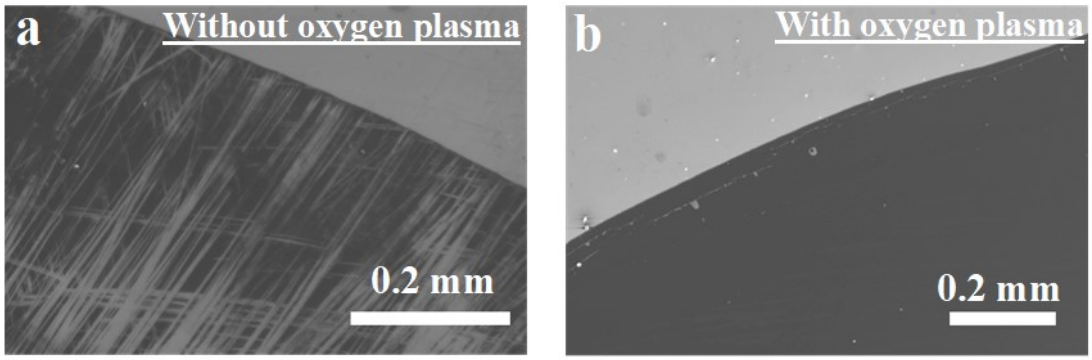

Fig. S1 The Ga_2O_3 films obtained by the squeeze-oxidation of Ga on the SiO_2/Si wafer without (a) and with (b) oxygen plasma cleaning.

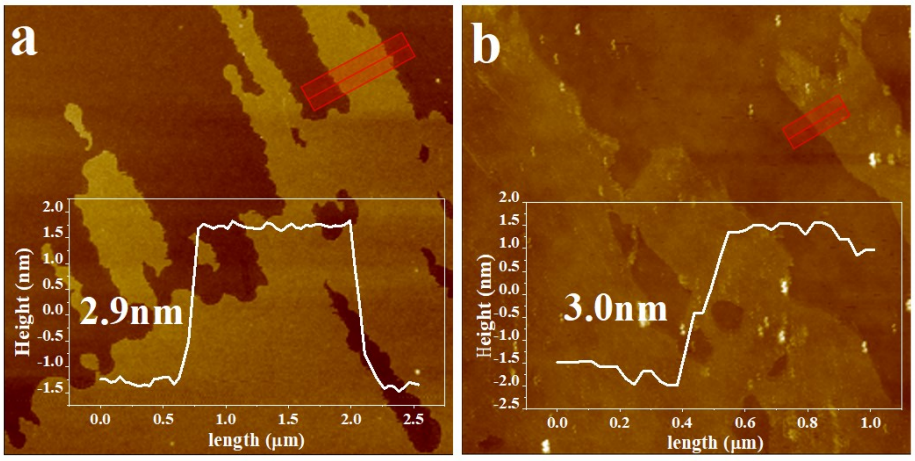

Fig. S2 AFM height profiles of the Ga_2O_3 films on the SiO_2/Si wafers fabricated by the oxidation under 50 °C for 1 min (a) and 5 min (b), respectively, which shows the thickness of the Ga_2O_3 film is independent of the oxidation time.

Thicker Ga_2O_3 film obtained from reprint method.

Repeating the squeeze-printing deposition process for three times, thicker Ga_2O_3 template film up to 8 nm can be obtained as shown in Fig. S3a. After the same nitridation process (10 sccm N_2 flow, under 800 °C for 20 min), GaN film with a thickness of ~ 0.9 nm was achieved as displayed in Fig. S3b. The thickness of the 2D GaN is independent of the thickness of the initial Ga_2O_3, which further supports the thinning of the template due to the nitrogen ion etching.

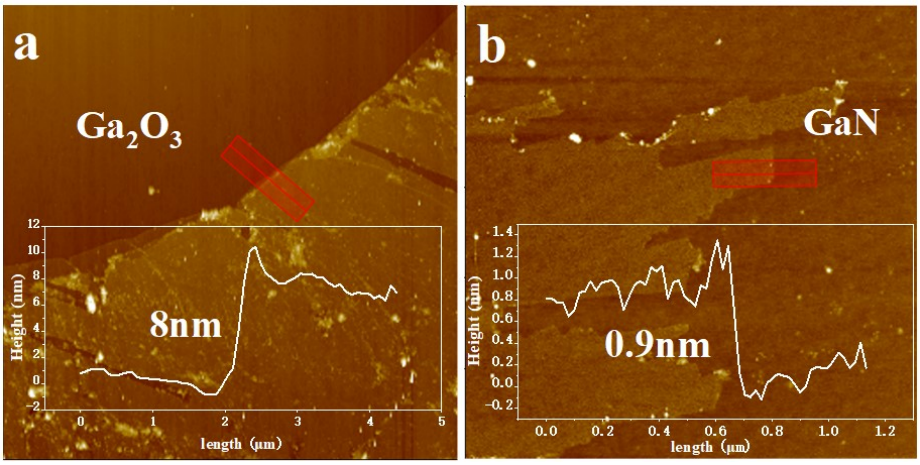

Fig. S3 AFM height profiles of (a) thick Ga_2O_3 film obtain from repeating the squeeze-oxidation process, and (b) the as-grown GaN nanosheet after N_2 plasma nitridation of the thick Ga_2O_3 film.

XPS of the Ga_2O_3 template

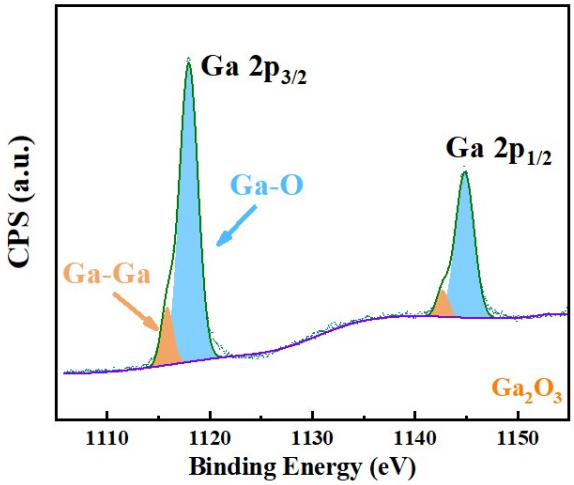

Fig. S4 XPS Ga2p spectra of the Ga_2O_3 film. The Ga-Ga peak marked in yellow suggests the residual Ga metal.

EDS of the GaN

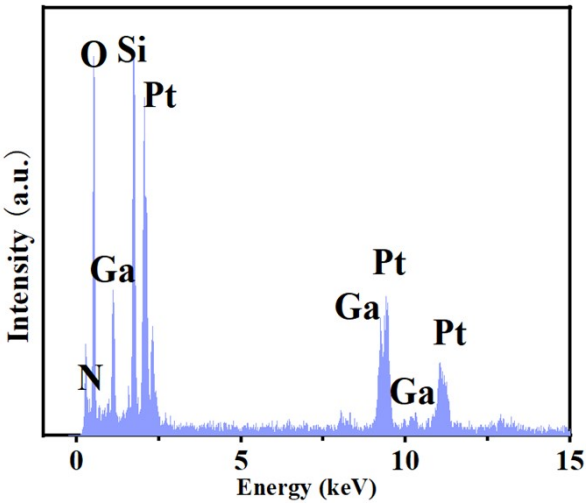

Fig. S5 EDS data of GaN region in Fig. 2g.

Preparation of 2D GaN on SiN_x grid for TEM Characterization.

The direct transfer of 2D GaN film from SiO_2/Si wafer to the TEM grid is challenging. Here, the Ga_2O_3 was firstly transferred onto the SiN_x grid through the van der Waals exfoliation method reported previously [4], where the Ga_2O_3 skin was exfoliated from the surface of liquid Ga by a SiN_x grid with gentle touch. Then the Ga_2O_3 on SiN_x sample was sent into PECVD for further nitridation. The nitridation process and growth condition is the same as that on the SiO_2/Si wafer. Eventually, 2D GaN nanosheet on SiN_x grid was fabricated successfully.

Etching effect of N_2 plasma

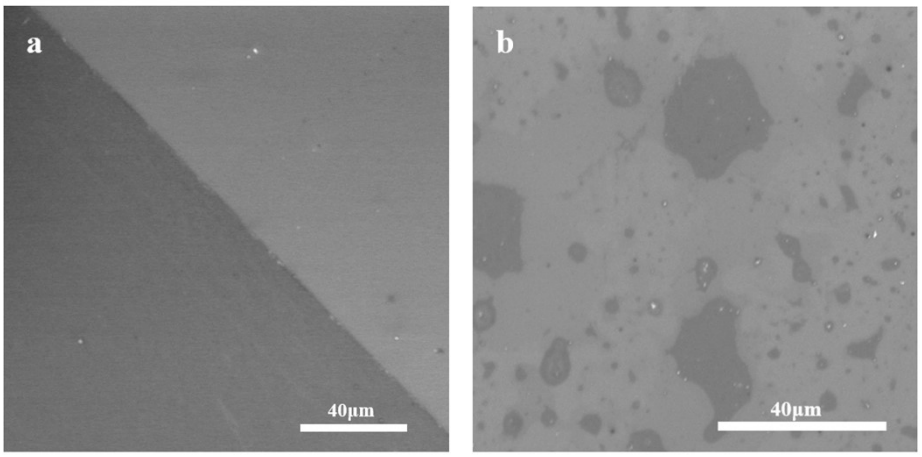

Fig. S6 SEM images of the GaN film with the reaction time for (a) 20 min and (b) 50 min, showing that the continuous film can be damaged into nanoislands owing to the severe etching effect of N_2 plasma.

The effect of Nitrogen gas flow and plasma power on the PECVD growth of 2D GaN

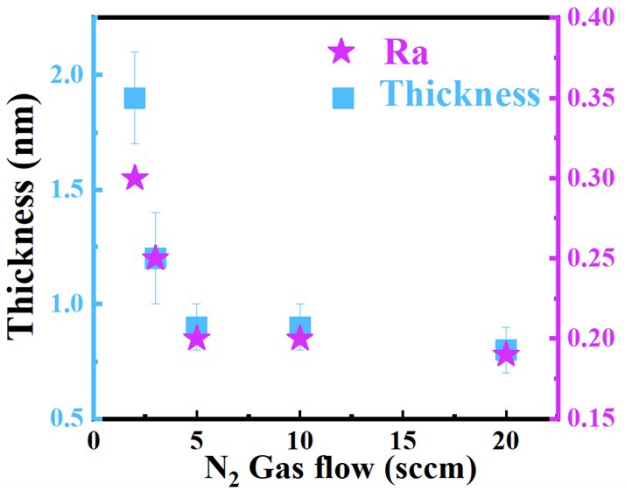

Fig. S7 Nitrogen gas flow-dependent thickness and roughness of the as-synthesized 2D GaN film. The growth time and the plasma power are fixed at 10 min and 10 W, respectively

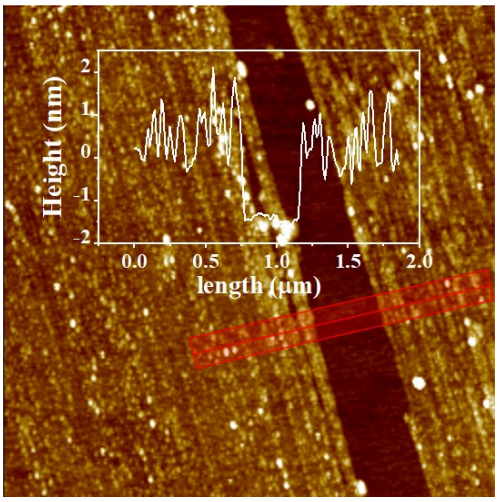

Fig. S8 AFM height profile of the GaN film under high plasma power (100 W) for 20 min.

Preparation of 2D GaN using urea as reactant through ambient pressure CVD

The Ga_2O_3 film on the SiO_2/Si wafer fabricated through the same squeeze-oxidation process was sent to the normal ambient pressure CVD (APCVD) system. Urea was applied as an ammonia precursor to react with Ga_2O_3 at 800℃ for 90min similar as previous reports [5]. Ar gas with a flow rate of 50 sccm was supplied as the carrier gas throughout the whole growth process. The thickness of obtained GaN film was ~ 2.8 nm as illustrated in figure S9a, the same as the Ga_2O_3 template. The XPS N1s and Ga 2p spectra show peak locations indicative for GaN, and no peaks associated with elemental Ga and Ga_2O_3 were observed (Figure S8 c-d). The O1s spectrum (Figure S8 e). of the GaN film show small Ga-O peak (marked in red) at 530.7 eV and large Si-O peak (marked in blue) at 532.3 eV, respectively. The non-negligible Ga-O peak could be attributed to a substantial fraction of nitrogen sites been substituted by oxygen atoms the in ambient air [6, 7]. The UV-vis spectrum (Figure S8 b) illustrated a ~ 3.3eV band gap of the GaN film, which is in consistent with the previous report using urea as nitrogen sources [5].

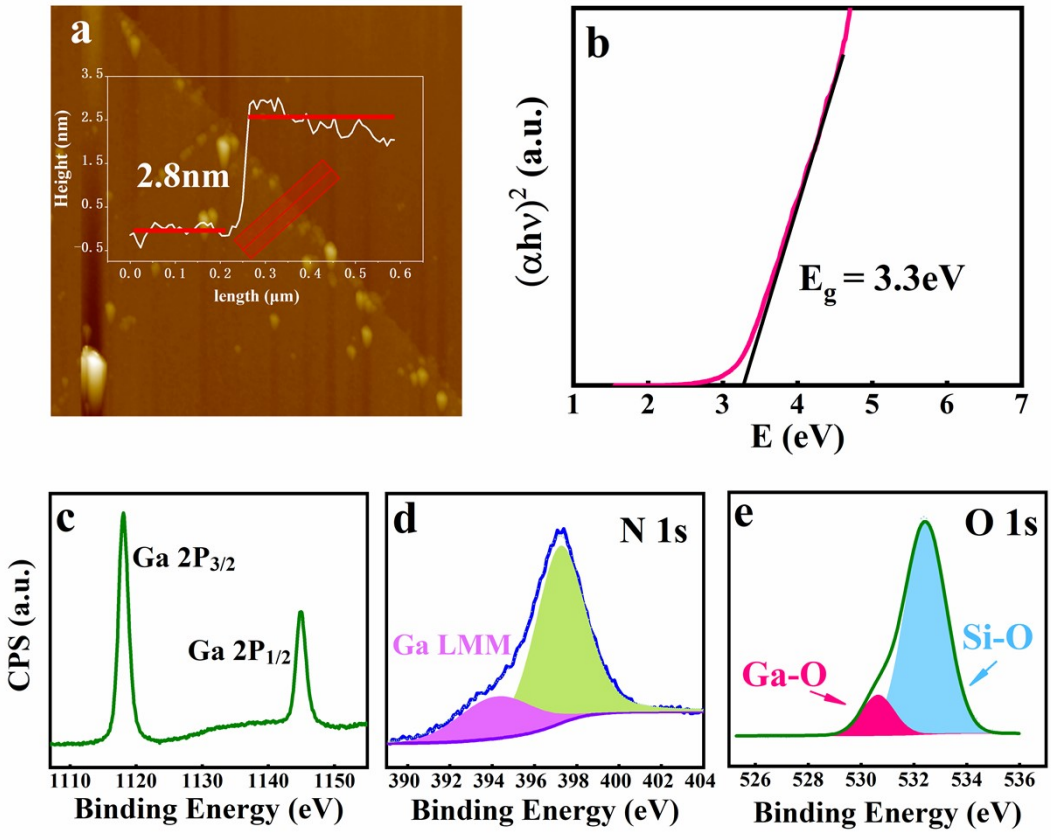

Fig. S9 (a) AFM topography and height profile of the GaN film nitridated using urea as nitrogen precursor through APCVD. (b) UV-Vis spectrum of the GaN film featured a 3.3 eV optical bandgap. (c-e) XPS Ga2p, N1s and O1s of the GaN film.

References:

1. A. Plech, U. Klemradt, H. Metzger and J. Peisl, *J. Phys. Condens. Matter*, 1998, 10, 971-982.
2. G. W. R. Leibbrandt, G. Hoogers and F. H. P. M. Habraken, *Phys. Rev. Lett.*, 1992, 68, 1947-1950.
3. N. Cabrera and N. F. Mott, *Rep. Prog. Phys.*, 1949, 12, 163-184.
4. A. Zavabeti, J. Z. Ou, B. J. Carey, N. Syed, R. Orrell-Trigg, E. L. H. Mayes, C. Xu, O. Kavehei, A. P. O'Mullane, R. B. Kaner, K. Kalantar-zadeh and T. Daeneke, *Science*, 2017, 358, 332-335.
5. N. Syed, A. Zavabeti, K. A. Messalea, E. Della Gaspera, A. Elbourne, A. Jannat, M. Mohiuddin, B. Y. Zhang, G. Zheng, L. Wang, S. P. Russo, E. Dorna, C. F. McConville, K. Kalantar-Zadeh and T. Daeneke, *J. Am. Chem. Soc.*, 2019, 141, 104-108.
6. T. Mattila and R. M. J. P. R. B. Nieminen, *Phys. Rev., B*, 1996, 54, 16676.
7. D. Kisailus, J. H. Choi and F. F. Lange, *J. Cryst. Growth*, 2003, 249, 106-120.