Ultrathin GaN Crystal Realized through Nitrogen Substitution of Layered GaS

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Abstract: GaN has been demonstrated as an important wide bandgap semiconductor in many applications, especially in optoelectronic and high-power electronics. Two-dimensional (2D) GaN, with enlarged bandgap compared to the bulk counterpart, not only amplifies existing functionalities but also opens up fresh possibilities for compact electronics. Although several methods have been developed to synthesize 2D GaN recently, their practical applications are hampered by either harsh growth conditions (e.g., high temperature and ultrahigh vacuum) or unsatifying performance due to grain boundaries. Here, we report the realization of few-nanometer thin GaN crystals via *in situ* atomic substitution of layered GaS flakes at a relatively low temperature (590 ℃). GaN with tunable thicknesses from 50 nm down to 0.9 nm (~two atomic layers) is achieved by applying the atomic substitution reaction to GaS with different numbers of layers. The obtained ultrathin GaN flakes retain morphology inherited from the GaS flakes and show high crystallinity from the transmission electron microscopy (TEM) characterization, while the thickness of GaN drops to about 72% of corresponding GaS flakes from the atomic force microscope (AFM) characterization. Time dependent mechanism study reveals both horizontal and vertical conversion paths with Ga_2S_3 as intermediate. Photoluminescence (PL) spectroscopy measurements show that the band edge PL of 2D ultrathin GaN is blue-shifted as compared with bulk GaN, suggesting the increased bandgap with the decrease of thickness. This study provides a promising method for obtaining ultrathin, high-crystallinity GaN with tunable thicknesses, utilizing a minimal thermal budget. This breakthrough lays a solid foundation for future investigations into fundamental physics and potential device applications.

Introduction

Two-dimensional (2D) materials serve as an exceptional platform for ground-breaking applications, owing to the unprecedented physics observable at the nanoscale.[1–4] Among these, van der Waals (vdW) materials are extensively studied, primarily due to the readily available access to high-quality 2D crystals.[5–12] Comparing with conventional vdW 2D materials, less study has been devoted to non-vdW group Ⅲ－Ⅴ 2D semiconductors. It's not until recently that atomically thin 2D crystals of a few three-dimensional binary compounds (e.g., GaN) are synthesized, which significantly broadens the range of 2D materials for multi-functionality.[13–19] When presented at 2D forms where quantum confinement effect manifests, dramatically different electronic properties from their bulk counterparts are observed.[15,20–22] For instance, the band gap of 2D GaN is predicted to blueshifted to 5.28 eV, compared with that of bulk GaN (E_g=3.4 eV),[23] which is also observed experimentally in ultrathin GaN prepared from migration-enhanced encapsulated growth (MEEG) technique utilizing epitaxial graphene[15]. Benefitting from the wide band gap and high electron mobility (2000 $cm^2/V/s$) of GaN, two dimensional electron gas in GaN based heterostructure has long been utilized for high-power and high-frequency optoelectronic devices.[24–27] In addition, GaN has demonstrated excellent performance in fabricating efficient blue and deep UV light-emitting diodes due to their wide bandgap . 2D GaN is of particular interest because the extreme quantum confinement effect offers additional tuning of the light-emitting properties.[28] Meanwhile, the ultrathin nature would bring mechanical flexibility to the devices and also open opportunities to integrate with existing 2D materials for unprecedented properties and applications. To this end, developing synthesis strategies for ultrathin GaN with high crystallinity, satisfactory area and controlled thickness is highly desired.

Epitaxial growth in molecular beam epitaxy (MBE)[29–32] and chemical vapor deposition (CVD)[33,34] processes are commonly utilized to produce large-area GaN films for industrial optoelectronic applications. Ideal substrate with minimum lattice mismatch for MBE synthesis is the GaN bulk crystals, which remains to be challenging and expensive to obtain.[35,36] Moreover, thin films created via MBE or metal-organic chemical vapor deposition (MOCVD) often present as small islands, fused together with abundant grain boundaries. These may influence the electrical properties of devices based on GaN. To harness GaN's full potential, there is a high demand for innovative technologies capable of producing superior quality GaN.[35,36] Besides conventional synthesis approaches, novel methods have been developed to prepared 2D GaN recently. Robinson and co-workers synthesize 2D GaN through a migration-enhanced encapsulation growth technique with epitaxial graphene.[15] However, the nanometer-size flakes pose tremendous chanllenge to fabricate electronic devices on such 2D GaN where poor mobility can greatly limit their practical applications.[37,38] Several other approaches utilizing surface-confined nitridation reaction strategies are developed to synthesize ultrathin GaN with relatively large areas. For instance, Daeneke and co-workers transfer ultrathin Ga_2O_3 films formed on the surface of liquid Ga droplets onto a substrate and further convert it into ultrathin GaN film through a nitridation reaction.[17] Although the as-prepared ultrathin GaN features large lateral dimensions up to several centimeters, the samples suffer from short range crystallinity, which will be the bottleneck for achieving high-performance electronics. As far as we know, for the reported methods, either the synthesis requires high temperatures above 800 °C (e.g. in liquid metal and graphene encapsulation methods), or the produced GaN films consist of small islands connected by a significant number of grain boundaries (e.g. in MBE and MOCVD techniques). These factors may adversely affect the electron mobilities in the material.[39–43]

Inspired by the atomic substitution approach we developed recently for ultrathin non-vdW materials,[19] we use vdW layered GaS as precursors for ultrathin non-vdW GaN through a nitridation reaction. In this process, the morphology of GaN is inherited from GaS flakes, and the thickness of GaN drops to 72% of the corresponding thickness of GaS. We observe both horizontal and vertical conversion paths which are more obvious in relatively thick flakes with Ga_2S_3 as an intermediate. More importantly, the obtained ultrathin GaN flakes are found to be highly crystalline, owing to the small lattice mismatch between GaS (3.587 Å)[44] and GaN[18] (3.323 Å). When compared to the bulk GaN, a significant blue shift in the band edge photoluminescence (from 3.5 eV to 3.7 eV) is discernible in the ultrathin GaN produced, indicating a wider band gap for this material. Leveraging the benefits of our methodology, our research paves the way for an expanded exploration of the science and applications related to ultrathin GaN.

Results and Discussion

Synthesis of Ultrathin GaN and Structural Characterization

Through atomic substitution of sulfur in GaS flakes with nitrogen, we obtain ultrathin 2D GaN crystals, which conventionally are challenging to access because of their non-layered structures (Figure 1a). The conversion process was performed in a tube furnace (Figure S1) at 590 ℃ through a gas-solid reaction between ammonia gas and GaS flakes. The ammonia gas is generated by purging Ar gas through ammonium hydroxide solution (~ 30%), after which the ammonia gas is carried by 200 sccm Ar gas through a dryer filled with KOH and CaO powers, where most of the moisture can be removed. Optical images of the flakes taken before and after the reaction show that the flakes retained their original morphology, while the optical contrast changed (Figure 1b, c), reflecting distinct absorption properties of the two materials.[32,45] After conversion , the flake

depicted in Figure 1c is characterized by AFM measurements (Figure 1d), revealing a 1.4 nm-GaN flake with smooth surface, as further substantiated by the height profile provided in Figure 1e. Raman spectroscopy measurements show the typical Raman features from GaS disappear after the reaction (Figure S2), indicating that the flakes have been converted into a different material, which is later confirmed to be GaN.

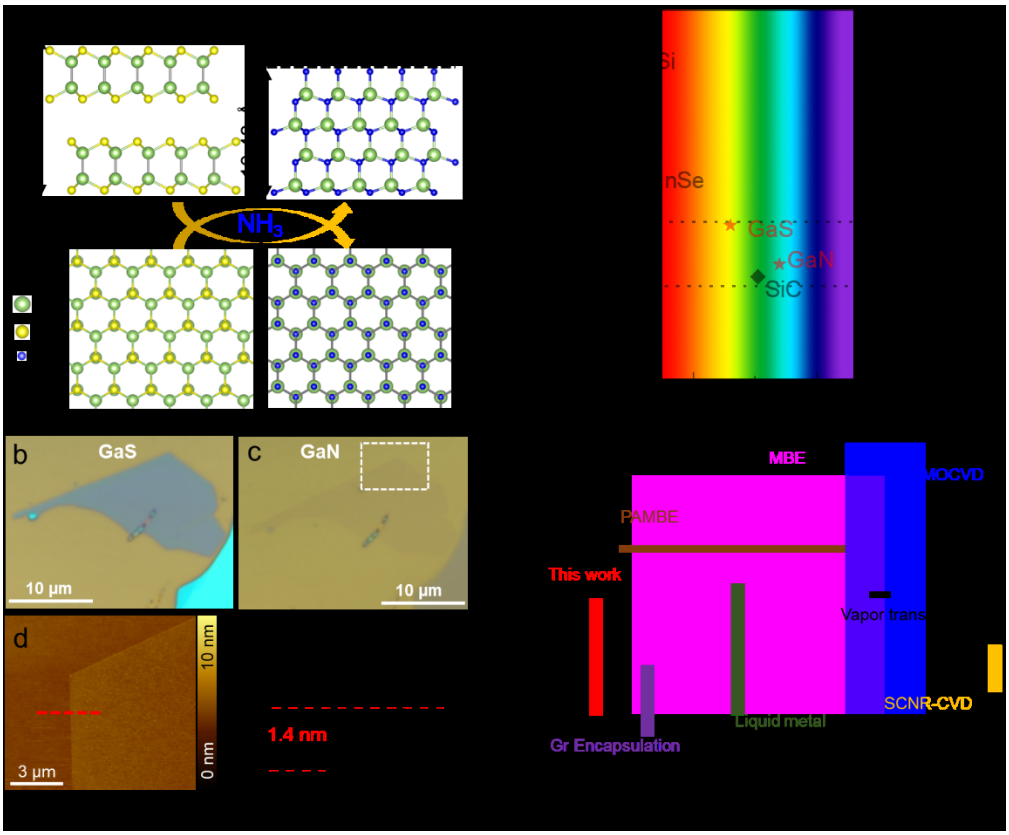

Figure 1. (a) Structure illustration of GaS and GaN; (b) Optical image of GaS; (c) Optical image of GaN converted from GaS in (b); (d) AFM image of the area highlithted by a white rectangle in (c); (e) AFM height profile measured along the red dashed line in (d); The thickness extracted from AFM is 1.4 nm; (f) Diagram of in-plane lattice parameter versus bandgap energy, establishing the possibility of probing deep into the ultraviolet regime with access to ultrathin 2D GaN. GaS and GaN in this work are highlighted with red stars. The dashed lines are to illustrate the potential substrates with lattice mismatch in the range of -4% to 12.7% from GaN. Si as the commonly used substrate is out of range which doesn't work well with the synthesis of GaN. (g) Comparison of processing temperature and accessible

thickness of GaN prepared through different approaches. Gr encapsulation: Migration-enhanced encapsulated growth (MEEG) technique utilizing epitaxial graphene;[15] Liquid metal: Ammonolysis of liquid metal derived 2D oxide sheets.[17] PAMBE: Plasma-assisted molecular beam epitaxy;[46,47] MOCVD: Metalorganic chemical vapor deposition;[48–53] MBE: Molecular beam epitaxy;[29–32,54–58] Vapor Transport: Infrared close space vapor transport;[59] SCNR-CVD: Surface-confided nitridation reaction via chemical vapor deposition.[18]

We attribute the successful synthesis of high-crystallinity ultrathin GaN to the smaller lattice mismatch with the GaS crystal precursor (see Figure 1f), as opposed to conventional substrates such as Sapphire or Si. Despite the contrast between the layered structure of GaS and the non-layered structure of GaN, the Ga atoms in both configurations display a hexagonal lattice. Furthermore, the lattice mismatch of GaS (3.627 Å) and GaN (3.216 Å)[18,44] is about 12.7%, a value comparable to the 15% lattice mismatch between GaN and sapphire (2.747 Å), which is a frequently utilized substrate for the epitaxial growth of GaN.[60] Consequently, high-crystalline ultrathin GaN crystals are realized through the nitrogen substitution of layered GaS. In contrast, the Si substrate exhibits a considerably larger lattice constant (5.431 Å), which often makes the direct deposition of high-quality 2D GaN film challenging, yielding samples of inferior quality with a high density of dislocations. Few successful attempts at the growth of GaN film on an Si substrate have been achieved, but these typically require the sacrifice of a buffer layer ranging from 300-900 Å.[61,62] Considering that a 12.7% lattice mismatch is still significant, an extensive amount of tension during the growth is anticipated. An additional advantage of our atomic substitution method, when compared to traditional epitaxial growth, lies in its ability to effectively dissipate the strain caused by the lattice mismatch between GaS and GaN, owing the van der Waals gaps present within the GaS layers. As a result, structural cracking during the reaction is averted due to the combined effect of the "relatively small" mismatch and the efficient dissipation of strain.

Therefore, the resulting ultrathin GaN flakes maintain the morphology and continuity of the original GaS flakes.

When contrasted with existing methodologies for synthesizing 2D or ultrathin GaN, our approach stands out due to its significant advantages, including the utilization of low-temperature processes (compared with MOCVD and liquid metal methods) and the provision of a wide array of thicknesses ranging from a few nanometers to tens of nanometers without sacrificing the grain sizes (Figure 1g). In Figure S3, we have shown some examples of atomic force microscope (AFM) images of GaN of various thicknesses together with their corresponding optical images. The low-temperature process not only saves the thermal budget in manufacturing, but also offers an opportunity to integrate GaN with other platforms through monolithic 3D integration technology without damaging exiting strucures on it, which has been demonstrated to be an advanced technology for large-scale circuits fabrication recently.[39–43] The effortless control over varying thicknesses of GaN paves the way to investigate the fundamental physical properties of GaN within the quantum confinement regime. This further provides an opportunity to uncover new functionalities for advanced electronic devices. Moreover, as it is potentially convenient to obtain large-area vdW GaS crystals using conventional 2D materials preparation methods (e.g., wafer scale CVD synthesis),[44] we anticipate our approach could lead to the achievement of large-area ultrathin GaN film, allowing further engineering for practical applications.

To gain insights into the atomic structure of the synthesized GaN, HRTEM measurements are performed by transfering GaS flakes directly onto a Si_3N_4 TEM grid for the conversion reaction followed by HRTEM characterization. Similar to GaN prepared on a SiO_2/Si substrate, the morphology of flakes retains while distinct optical contrast is observed after conversion (Figure S4). Figure 2a shows a typical low magnification TEM image of a GaN flake, showing smooth

surface of the whole flake. A zoom in HRTEM image (Figure 2b) of the area highlighted with yellow square in Figure 2a clearly displays the crystalline structure of GaN and a distance of 0.29 nm between two adjacent lattice planes matching well with the distance between (100) planes in wurtzite GaN.[18] Compared with bulk GaN (0.279 nm), the distance between (100) planes of our ultrathin GaN is about 4% larger, which is attributed to the strain induced into the lattice during the structure transformation.[20,21,63] When GaN is thinned down to region where the surface playes an important to stabilize the structure, they tend to expand in lateral direction in order to remove the destabilizing dipole.[22,63] Specifically, ultrathin films of GaN usually have a polar surface, leading to the divergence of the surface energy that makes the surface intrinsically unstable. To stabilize the polar surfaces, wurtzite structures commonly adopt a structural relaxation process where the geometry of surface atoms is altered away from sp^3 orbital hybridazation towards a sp^2 trigonal planar geometry as the bond lengths reduce and the angles increase. The SAED pattern shows a hexagonal lattice of the crystal over the entire flake, further confirming the wurtzite structure of the obtained GaN (Figure 2c). Importantly, SAED patterns taken at four different locations on the flake show identical orientation, suggesting single crystallinity across the whole flake (Figure 2c). In addition to the main hexagonal SAED pattern, other diffraction peaks were observed with varying brightness depending on the thickness of the flake, which matches well with the SAED simulation results (Figure S5). Energy-dispersive spectroscopy (EDS) is further performed on a relatively thick GaN flake under SEM mode where N and Ga signal was observed and no S signal remains, indicating a complete conversion from GaS to GaN. Raman mapping is conducted to verify the uniform and complete conversion from GaS to GaN. Before conversion, Raman map of GaS shows uniform intensity distribution of A^1_{1g} peak (Figure S6a), while no A^1_{1g} signal is observed after complete conversion (Figure S6b). Figure 2d shows a SEM image of a

GaN flake with smooth surface, and its EDS elemental maps of Ga (Figure 2e) and N (Figure 2f) reveal uniform distribution of elements in the flake, suggesting great sample quality prepared by the atomic substitution method.

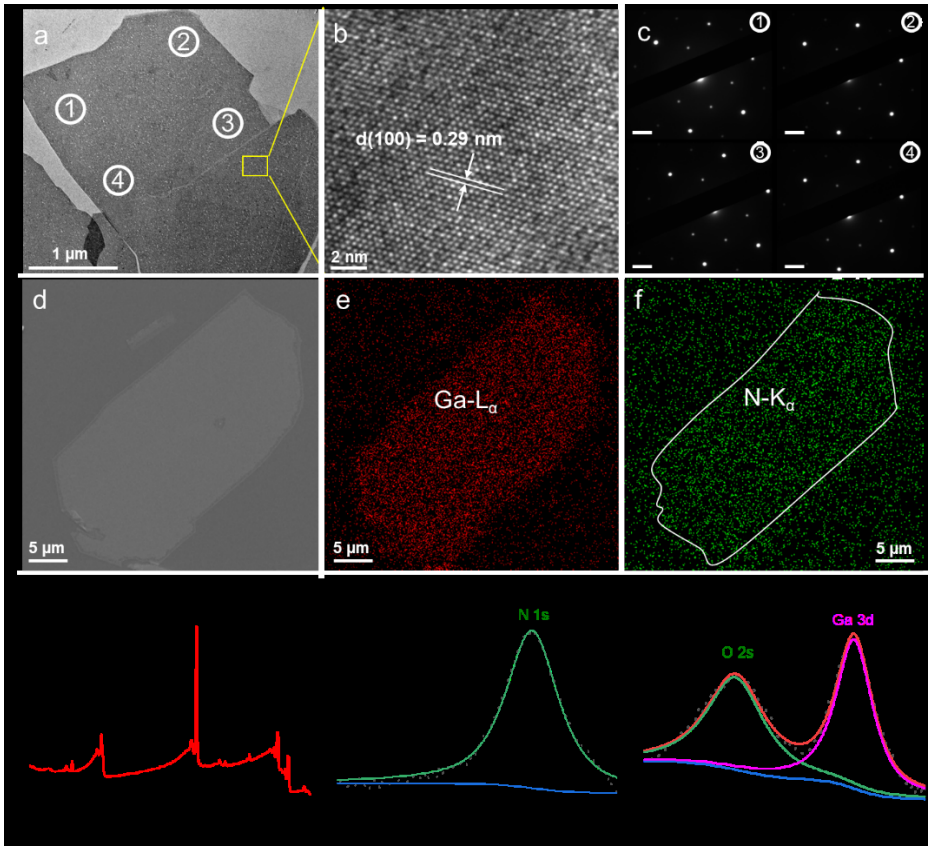

Figure 2. Crystal structure and elemental analysis of GaN converted from GaS; (a) Low magnification TEM image of GaN; (b) HRTEM image taken on the area indicated by yellow square in (a); (c) SAED patterns of an as-prepared GaN flake measured at different locations as indicated by white circles in Figure 2a. Scale bar: 5 1/nm. (d) SEM image of a GaN flake. (e, f) EDS elemental maps of Ga-Lα (e) and N-Kα (f) elements in the flake shown in (d). White line in (f) depicts the contour of the GaN flake shown in (d). (g) XPS survey scan of GaN; (h, i) XPS fine spectra of N 1s (h) and Ga 3d (i) core level peaks of GaN. O 2s is present due to the SiO_2/Si substrate. Spectra fitting lines and baslines (in blue) are shown in (h) and (i).

Investigation of the Conversion Mechanism

Upon substituting S in GaS with N, the vdWs gaps are removed as N forms covalent bonds which connect the Ga atoms between two adjacent layers. In theory, the height of four layers of Ga (one unit cell in GaS) drops from 13.786 Å to 10.48 Å (two unit cells in GaN) according to the crystal structures of GaS and GaN (Figure 1a). Therefore, we expect a thickness decrease when GaS is converted to GaN by about 24%. To validate this hypothesis, we perform AFM to measure the thickness of flakes before and after conversion. Indeed, we observe that the thickness of GaN decreases compared with that of corresponding GaS. Figure 3a and 3b show an example of thickness change characterized by AFM, where two GaS flakes with thicknesses of 32 and 22 nm (Figure 3c) are converted to GaN flakes with thicknesses of 23 nm and 15 nm (Figure 3d), respectively. Additionally, by ploting the thickness of GaS with respect to GaN ranging from a few nm to ~ 80 nm (Figure 3e), a linear correlation is established between the thickness of GaS before conversion and GaN after conversion. Pearson correlation analysis in Figure S7 proves that the experimental and theoretical thickness difference are strongly correlated (r = 0.87). Ratios of GaN/GaS are ploted, yielding a horizontal trendline at 72%, suggesting a thickness decrease of 28% after conversion, which aligns well with the theoretical predication of 24%. The small deviation (~ 4%) from theoretical value may originate from the uncertain gaps between flakes and the SiO_2/Si substrate, which can be predominant especially for thin flakes. When comparing the experimental thickness difference (y_1) between GaS and GaN with the theoretical values (y_2) (Figure 3f), we observe a well agreement as shown by the small deviation between y_1 and y_2, which is also excellently demonstrated by the ratio of y_1/ y_2 being close to 1. This trend persists for both thin and thick flakes encompassing various numbers of layers, given that a uniform conversion method is adhered to during the transformation process.

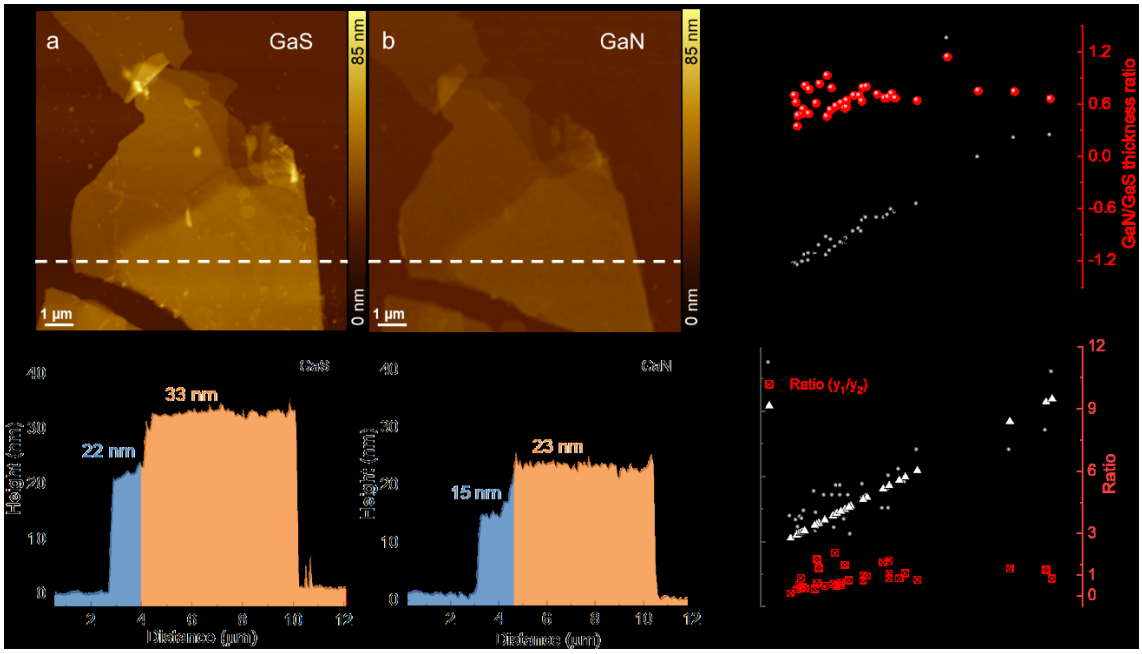

Figure 3. (a, b) AFM images of GaS before conversion (a) and GaN after conversion (b); (c, d) AFM height profiles extracted from GaS (c) and GaN flake along the white dashed lines shown in (a) and (b), respectively; (e) Correlation plot of the thickness of GaS and converted GaN (in black). Data points in red show the corresponding thickness ratios of GaN/GaS; (f) Layer dependent thickness study of the conversion from GaS to corresponding GaN. The number of layers is calculated through the thickness of GaS. Theoretical thickness difference $y_2 = N\times(d_{GaS} - d_{GaN})$, where N is the number of layers of GaS; d_{GaS} is the thepretical thickness of single layer GaS; d_{GaN} is the theoretical thickness of single layer GaN. Experimental thickness difference y_1 = Experimetnal thickness of GaS – Experimental thickness of corresponding GaN (converted from the same GaS).

In order to unravel the conversion mechanism, we scrutinized the evolutionary changes in the structure throughout the conversion process. This was achieved by conducting thorough characterizations of the flake at various stages of the reaction. The multistep conversion is conducted at lower reaction temperature (~ 580 ℃) on a relatively thick flake (~35 nm) in the pursance of better visulization. Following each step, we take the sample out and take optical images of the extact same flake. As shown from Figure 4a to 4f, the converted area (darker contrast) labeled by white arrows expands with time accompanied by diminishment of unconverted area

(brighter contrast), suggesting the progressive conversion from GaS to GaN via Ga_2S_3 intermediate. As an example, the optical contrast of the whole flake after 1 hour reaction (Figure 4b) is drastically distinct from original GaS flake (Figure 4a) where the majority area (darker contrast) remains to be Ga_2S_3 as confirmed by Raman spectra as both A_{1g} and F_{2g} vibrational mode from Ga_2S_3 are observed (Figure 4g).[64] TEM images of both the unconverted and converted areas present distinct electron diffraction patterns from Ga_2S_3 and GaN, thereby corroborating our observations (as depicted in Figure S8). The converted region of the thicker flake exhibits a darker contrast, and its Raman spectrum aligns with that of GaN. After a duration of 4.5 hours, the entire flake is thoroughly converted, as evidenced by the uniform optical contrast across it. It is also worth mentioning that the reaction rate will increase significantly at elevated temperature (e.g. 590 ℃) and fully conversion can be realized at shorter period of time (~ 1 h). Nevertheless, when the reaction temperature is increased further, such as to 600 ℃, the appearance of cracks becomes more prevalent, a phenomenon possibly caused by the enhanced substitution rate at this higher temperature, as illustrated in Figure S9. Comparing reaction for 1 hour at different temperatures further confirms the strong temperature dependence of the conversion from GaS to GaN. The Kelvin probe force microscope (KPFM) measurements corroborate our observation with morphology and surface potential information. Although the AFM height image shows the surface is very uniform over the whole flake with a roughness of 1.5 nm in an intermediate state of the conversion (Figure 4h), the surface potential varies drastically after the conversion. Figure 4i and 4j show KPFM work function and surface potential image of the flake after 1.5 hour conversion shown distinct work functions between converted areas (GaN) and unconverted areas (Ga_2S_3), matching well with the observation from optical images. The area with larger conversion degree (iii in Figure S10) shows higher surface potential as opposed to area with less conversion degree

(i, ii in Figure S10). We evaluate the morphology by extracting the surface root mean square (RMS) roughness of the flake and plotting it over reaction time, where negeligible rougness change has been observed (Figure 4k). Additionally, we have charted the conversion percentage from Ga_2S_3 to GaN based on the areas of each compound depicted in the optical images from Figure 4a through 4f. In the initial three hours, the converted area expands rapidly relative to the reaction time, whereas the subsequent 1.5 hours reveals only a minimal change in the converted area as the conversion nears 100%. We attribute the Ga_2S_3 intermediate to the lower standard Gibbs free energy of formation of Ga_2S_3 around the conversion temperature (~ 580 ℃).[65] Despite the absence of external S source, nucleation of Ga_2S_3 can be still realized by enrichment of S locally from GaS (Figure 4l), which is more thermodynamically favorable. Eventually with the flow of NH_3, S is carried out and Ga_2S_3 (Figure 4m) will gradually be converted to GaN (Figure 4n) when NH_3 of high vapor pressure takes over. It's worth mentioning here that the size of NH_3 molecule (3.26 Å) is smaller than the gap between GaS layers (4.07 Å), which allows for free diffusion, enabling the conversion of the interior and exterior areas of GaS (Figure S11).

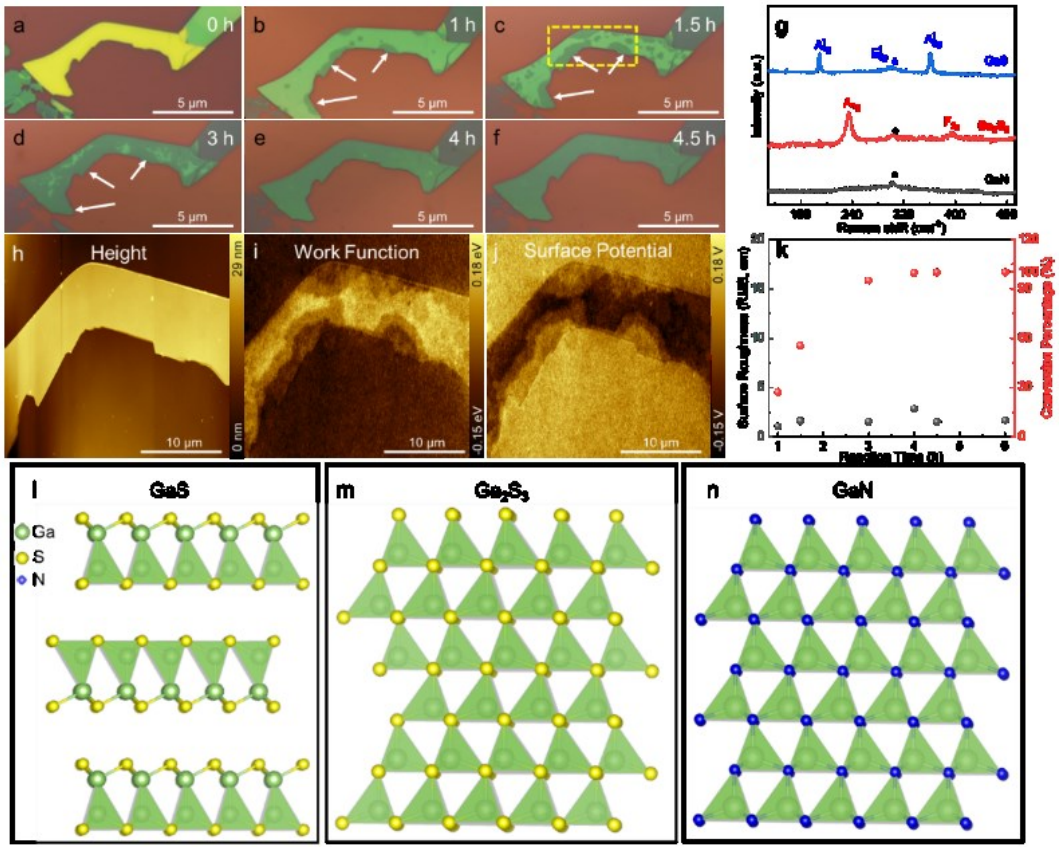

Figure 4. Mechanism study of the conversion from GaS to GaN. (a-f) Roadmap of optical images taken at different stages of the conversion process from GaS to GaN with Ga_2S_3 as intermediate. The white arrows indicate the areas with darker contrast that are converted from Ga_2S_3 to GaN; (g) Raman spectra of GaS, Ga_2S_3 and GaN. The peaks labeled with * are from the SiO_2/Si substrate; (h-j) Height (h), work function (i) and surface potential (h) images obtained from KPFM measurements of the area highlighted with yellow rectangle in (c); (k) Conversion percentage plot of GaS to GaN at various stages (in red) and surface roughness study (in black). The conversion percentage is calculated by comparing the area with darker contrast shown in optical images at different conversion time over the area of the whole flake. Surface roughness is extracted from height profile of the same area of various conversion stages as highlighted in yellow rectangle shown in (c); (l-n) Polyhedral structure illustration of GaS (l), Ga_2S_3 (m) and GaN (n), respectively.

Moreover, we have noted varying reaction dynamics between thin and thick flakes. Based on optical images, thin flakes undergo conversion to GaN within one hour at 580 °C. However, thicker

flakes require a longer duration to achieve full conversion, as demonstrated by the non-uniform optical contrasts at different areas of the flake (see Figure S9a and S9b). The progression of the converted area over time, coupled with the rate discrepancy between thin and thick flakes, suggests that the conversion process might proceed in two directions: both horizontally and vertically. Horizontally, converted area initiates from edge area where defects and dangling bonds present with higher abundance, then gradually expands from edge to central area of the flake. Vertically, thin flakes with a smaller number of layers finishes conversion within shorter time compared with thick flakes. Both GaS and Ga_2S_3 coexist in converted area of thick flakes, implying that the reaction starts from top surface inward to the bottom. Hence when the reaction is incomplete, the top part of the flake is Ga_2S_3 and GaN while the bottom part remains to be GaS. It is reasonable to believe that vertical reaction is the rate limit step, as thinner flakes convert within a shorter period of time where no vertical heterostructure is observed. Low magnification TEM image in Figure S12a shows a thin flake of GaN with smooth surface. SAED of the area (Figure S12b) confirms the high crystalline feature of GaN with only one set of diffraction pattern. We utilize x-ray photoelectron spectroscopy (XPS) to investigate the chemical composition and oxidation states of the GaN samples. The survey scan spectrum from the XPS analysis in Figure 2g reveals the presence of Ga, N from GaN sample and C, O, Si which are either from the SiO_2/Si substrate or from the environment. The broad N 1s peak centered at ~ 397.6 eV corresponds to the binding energy of N in GaN.[15,17,66] In Ga 3d region, both Ga 3d and O 2s (from SiO_2/Si) are observed since their binding energies are close.[17] It is worth mentioning here that no residual S peaks associated with GaS is observed (Figure S13),[64] which is expected for the full conversion from GaS to GaN.

Enlarged Bandgap of 2D GaN Revealed by PL Study

To determine the optical band gaps of the obtained ultrathin GaN with various thicknesses, we further measured the PL emission spectra using 266 nm laser excitation. As shown in Figure 5a, pronounced PL signals were observed from samples from 25 nm down to 4.4 nm. Importantly, the emission energy blue shifts from 3.5 eV for the 25 nm thick sample to 3.7 eV for the 4.4 nm thick sample with the decrease of sample thickness, suggesting the increase of the optical band gap of GaN. The results match well with the theoretical prediction on the band gap enlargement of 2D GaN.[15] Note that a 5.28 eV band gap was predicted for a single layer GaN in literature,[15] we did not observe the PL signals from thiner samples, probably due to the weak signals. We plot the band gap against the thickness of six samples in Figure 5b, where an evident blue shift with decreasing thickness exhibits the signature of quantum confinement effect in the 2D limit. By using GaS precursors of different thicknesses, we successfully engineered optical band gaps of GaN flakes of various thicknesses using our atomic substitution approach. In addition, we observed typical red defect emission at around 620 nm from the obtained GaN (Figure S14), which has been widely reported in GaN synthesized using many other methods as the C and O doping induced defect emission.[54,59,67]

The thickness-dependent PL can be understood more quantitatively by examining the excitonic peak position with an intuitive model that involves quantum confinement and exciton binding energy as well as Bohr radius. To extract the Bohr radius, we plot the PL peak position of exciton E_c of the as prepared GaN flakes with various thickness. We find that flakes with thickness larger than 11 nm has a linear dependence on $1/L^2$, which can be fitted by the conventional model of infinite quantum wells as:[68,69]

$$E_c = E_g + R_y + \frac{\Pi^2\hbar^2}{2mL^2} - R_y \text{ ..... } eq.\ (1),$$

where L is thickness of GaN flake, E_c is the exciton peak position, E_g is the excitonic resonance energy in bulk GaN, R_y is the exciton binding energy and assumed not changing with the thickness in the model of infinite quantum wells, and m is the reduced electron-hole effective mass of the flake. The fitting to the experimental results yields:

$$E_c = 3.336\ \text{eV} + \frac{82.54}{L^2} \quad \ldots\ldots\ldots eq.\ (2),$$

from which we can derive the reduced effective mass $m = 0.457\ m_0$ for the exciton in GaN flakes that are thicker than 19 nm. Based on the fitting results, we can also derive the exciton binding energy R_y = 78 meV and the Bohr radius a = 1.03 nm, which is in the same order of reported Bohr exciton radius (2.5 nm) for GaN,[70–72] in which the static dielectric constant is set to be 8.9 as measured for bulk GaN previously.[70,73]

The peak position of exciton E_c of GaN flakes thinner than 19 nm shows apparent deviation from the model of infinite quantum wells. Instead, we can fit the experimental results with a model of quantum wells with fractional dimensional space as:

$$E_C = E_g + R_y + \frac{\Pi^2\hbar^2}{2mL^2}[(D-1)/2]^2 - \frac{R_y}{[(D-1)/2]^2} \ldots\ldots\ldots\ldots\ldots\ldots eq.\ (3),$$

where D is the effective dimensionality defined by the ratio of the exciton binding energy in the GaN flakes (R_y*) and that of bulk GaN (R_y) as:

$$[(D-1)/2]^2 = R_y / R_y^* \ldots\ldots\ldots\ldots\ldots\ldots eq.\ (4).$$

The factor of $[(D-1)/2]^2$ originates from the change in the effective mass associated with the effective dimensionality. For the flakes thicker than 11 nm, D is 3 and *eq.* (4) is reduced to the equation for infinite quantum wells. By fitting the experimental results with *eq.* (4), we obtain the effective dimensionality D of 1.83, 2.28, 2.48, 2.74 for GaN flakes with thickness of 4.4 nm, 8.8

nm, 11.5 nm, 19 nm, respectively. We then derive the corresponding exciton binding energies using *eq*. (4) to be 0.453 eV, 0.19 eV, 0.142 eV and 0.103 eV for the corresponding GaN flakes; we also derive the corresponding Bohr radius of excitons from $a_b^* = a_b(D-1)\ /\ 2$ as 0.42 nm, 0.66 nm, 0.76 nm and 0.90 nm, respectively. The variantion of Bohr radius and exciton binding energies suggest that the thickness of the GaN can be utilized as an important knob to tune the optical and electronic properties of GaN.

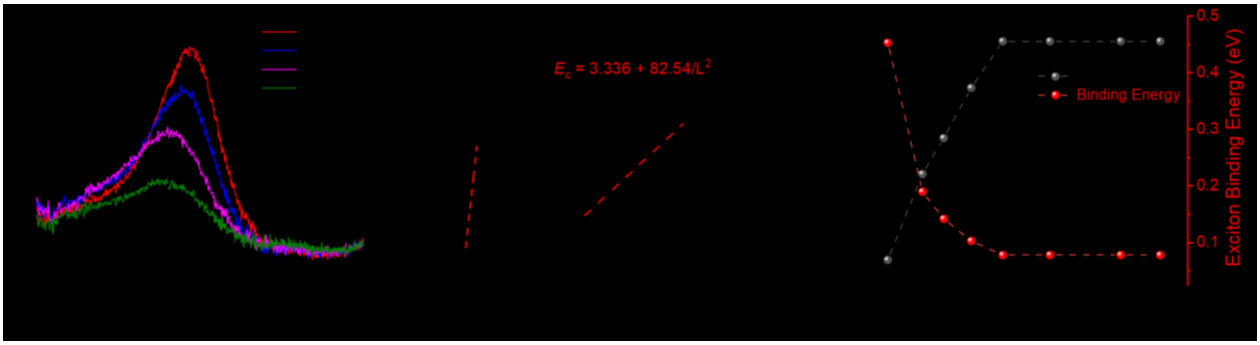

Figure 5. Thickness dependent PL of GaN. (a) PL spectra of four GaN samples with different thicknesses; (b) Layer dependent excitonic effect in as prepared GaN flakes; The position of the PL peak in GaN as a function of $1/L^2$, where L is the thickness of the film. The red line is the fitting result using the model of infinite quantum well with the fitting equation given as shown. The inset is a magnified version of the area indicated by the dashed red rectangle; (c) The dependence of the binding energy and exciton radius in GaN flakes on the sample thickness.

Conclusion

In conclusion, we have successfully fabricated ultrathin GaN nanosheets through the process of nitrogen substitution in GaS at a moderately low temperature of approximately 590 ℃. By capitalizing on the readily accessible van der Waals (vdW) layered structure of GaS precursors with a range of thicknesses, we have devised a straightforward method to create high-quality, ultrathin 2D GaN. This method further allows for thickness tuning down to sub-nanometer levels. Through our exploration of the time-dependent conversion process, we have unveiled a conversion

mechanism from GaS to GaN that involves Ga_2S_3 as an intermediary stage. The optical bandgap of our ultrathin GaN was identified through photoluminescence (PL) measurements, revealing an enlarged bandgap in comparison to the bulk form. Thickness dependent quantum confinement effect is also studied through examing the Bohr radius and exciton binding energy. We assert that the benefits of our atomic substitution strategy could present extensive opportunities to delve into both the fundamental science behind ultrathin GaN, and its potential applications in device technology.

ASSOCIATED CONTENT

Supporting Information

Full experimental details, data associated with the GaN synthesis, optical images, Raman Spectra, AFM (KPFM) analysis, PL spectra, SEM, TEM and XPS characterizations.

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Notes

The authors declare no competing financial interest.

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