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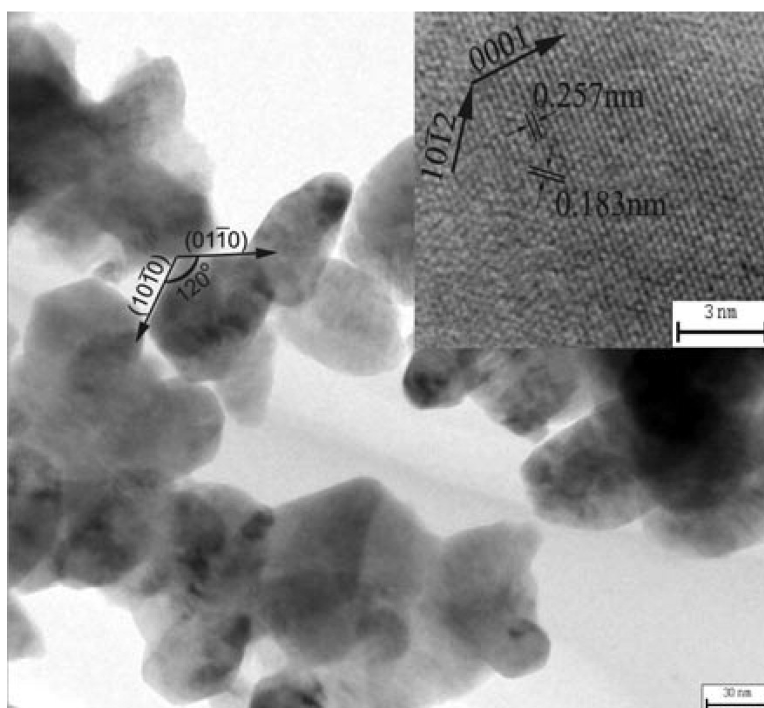

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Route to GaN and VN Assisted by Carbothermal Reduction Process

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Metal nitrides are among the important materials that find wide applications from optoelectronic devices to high-temperature coatings.[1] GaN, for example, has been recognized as one of the most important semiconductors in the fabrication of blue LEDs and LDs.[2] Conventionally, metal nitrides are made by the direct reactions of metals with ammonia or nitrogen at high temperatures (≥1000 °C).[3] An effective and low energy consuming route, solid-state metathesis (SSM), has been developed for synthesizing nitrides over the past decade.[4] The precursors are usually the metal halides and the alkali nitrides in these reactions. The driving force for the reactions comes from the formation of the stable alkali or alkaline earth halides that are very thermodynamically favored. The exothermic energy makes the reactions self-propagate to completion. However, the temperatures are usually as high as 1100 °C, leading to the decomposition for some nitrides, such as GaN.[5] Other existing methods, such as metal amide decomposition,[6] nonaqueous solvothermal reactions,[7] and carbothermal reduction processes,[8] suffer various drawbacks such as poorly crystallized, low yields, and high energy consumption to some extent. Consequently, new solid-state routes are still desired to prepare metal nitrides.

Carbon nitride materials have been the focus of materials research for the past decades due to their possible high hardness comparable to diamond.[9] Recently, by a facile mechanochemical method, we prepared the amorphous carbon nitride (a-$C_3N_{3.69}$) with the atomic ratio of 1.23 for N to C.[10] In this communication, we report a solid-state route to GaN based on a modified SSM reaction. Here, however, we choose a-$C_3N_{3.69}$ as a precursor with another one being an oxide to form an SSM reaction. This reaction might be enhanced by the formation of carbon monoxide and nitrogen byproducts that are much more stable than the precursors. GaN and other nitrides are expected to be obtained in a much softer condition by this route. Our experiments show that the route allows one to nitridize the gallium oxide into GaN at 650 °C. This route can be extended to prepare other nitrides. VN nanocrystals are also synthesized by using V_2O_5 and carbon nitride at 850 °C. A-$C_3N_{3.69}$ is found to play double roles as both carbonizing and nitridizing agents in these reactions. The details of the preparation procedure are as follows:

In a typical run, 0.17 g (1.94 mmol) of as-synthesized $C_3N_{3.69}$ and 0.12 g (0.638 mmol) of Ga_2O_3 (the molar ratio is about 3:1 for $C_3N_{3.69}$ to Ga_2O_3, here, we used 2-fold excess of the $C_3N_{3.69}$ material to ensure the complete conversion of Ga_2O_3 to GaN) are mixed and grounded together, and then pressed to a pellet, followed by placing into a silica ampule with the volume of 10 cm^3. Second, the ampule with the pellet is evacuated to 3×10^{-6} Pa and sealed while heating at 100 °C. In succession, the ampule is kept at 650 °C in an oven for 8 h. At last, the ampule is cooled naturally to room temperature. Large-scale gray powder is obtained after the reaction. In addition, black particles were found on the inner surface of the ampule. ***Warning***: appropriate quantity of the reactant mixture should be adopted to avoid possible explosion due to high pressures.

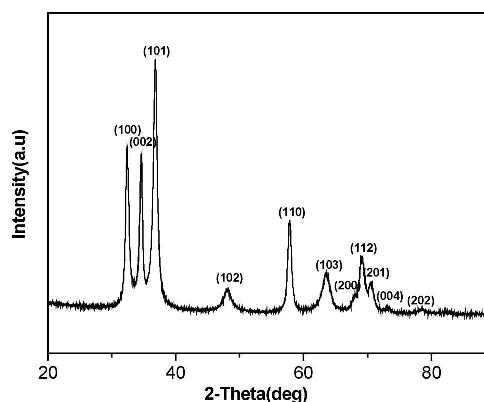

Figure 1. XRD pattern of the GaN product.

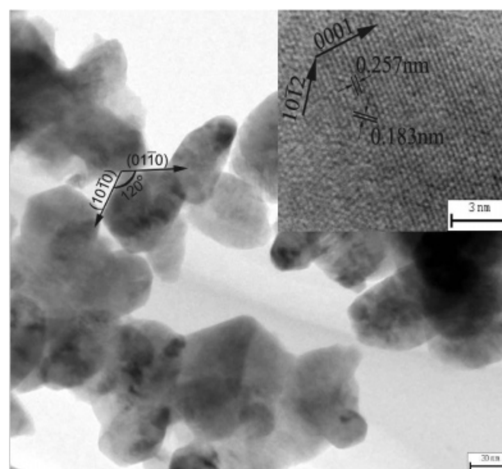

Figure 2. TEM image of the GaN nanocrystallites; inset is the HRTEM image of the lattice.

Energy-dispersive X-ray analysis (EDX) shows that the product consists of Ga, N, and O elements, and the black particles on the inner surface carbon element. The O element probably comes from the O_2 and H_2O absorbed on the surface of the sample. The X-ray diffraction (XRD) pattern (Figure 1) shows that the products are hexagonal GaN without any trace of impurity phase under the instrument's resolution. The indexed pattern agrees well with the ICDD-PDF #50-0792, only with 10% higher intensity for the (002) peak, probably due to a small amount of O inclusions. The broadening peaks indicate that the grain sizes are on the nanometer scale, as confirmed by the TEM observations.

The TEM image reveals the product consists of well-crystallized nanoparticles with sizes ranging from 30 to 50 nm; see Figure 2.

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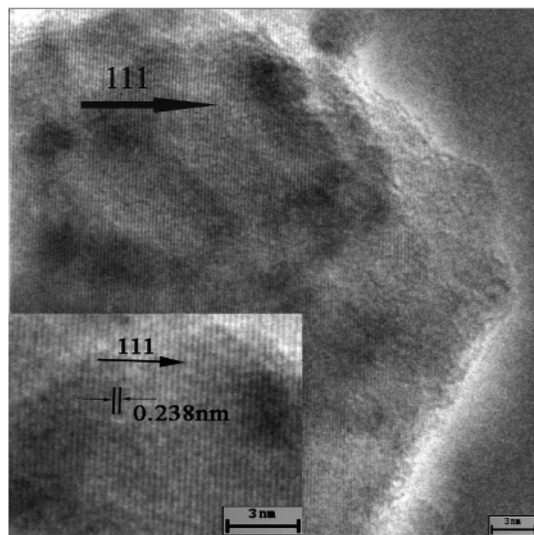


Figure 3. HRTEM image of the VN crystallite; inset is the amplified lattice image.

Shown in the inset is the HRTEM image of the lattice. The lattice spacings are 0.257 and 0.183 nm for (002) and (102) planes, respectively, giving further evidence that the product is hexagonal GaN. From their regular morphologies, we speculate that the nanoscale GaN particles form in conditions close to the equilibrium state in the synthesizing process. The growth speed is estimated to be about 5 nm/h.

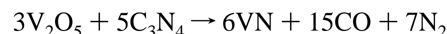
The route reported here is applicable to prepare other nitrides. By a similar method, we synthesized the VN powders at the reacting temperature of 850 °C, with the molar ratio of 8:1 for $C_3N_{3.69}$ to V_2O_5. The addition of more excess of $C_3N_{3.69}$ is to prevent the unreacted V_2O_5 in the product. For the VN product, besides the V, N, and O elements, EDX shows a trace of C element; this is probably due to the byproduct of the decomposed carbon nitride at high temperatures.

XRD measurements indicate that the products are cubic VN (see Supporting Information). Broadening peaks are also observed in this case. The average size estimated by the Sherrer formula is about 20 nm. However, the HRTEM image (Figure 3) does not show clearly the size of the particles because of the severe particle aggregations. Nevertheless, the amplified image shown in the inset does indicate the spacing of 0.238 nm for d_{111}, in good agreement with the known value for cubic VN (ICDD-PDF #78-1315). The obtained VN crystallite is irregular in shape compared with GaN.

In addition, besides GaN and VN, we have obtained other metal nitrides, such as CrN, W_2N, and AlN, by the reactions of Cr_2O_3, WO_3, and Al with the a-$C_3N_{3.69}$ in similar manners. The details of the synthesis of these nitrides will be reported elsewhere. These facts suggest that the route is effective in synthesizing a variety of nitrides. We note that Al_2O_3 cannot be converted into AlN by a-$C_3N_{3.69}$, while metal Al can. However, this provides useful clues to understand the reaction mechanism. A-C_3N_4 is known to decompose into various carbon nitride species, such as $C_2N_2^+$, $C_3N_2^+$, and $C_3N_3^+$, at temperatures above 550 °C.[11]

The overall pathway is expected to involve a two-step process: a carbothermal reduction-like process and a nitridizing process. First, these species which are very chemically active will easily bond the oxygen atoms and reduce the metal oxides into metals. Then, the subsequent nitridizing reactions of the metals with the nitrogen atoms will occur and finally lead to the formation of nitrides. The overall chemical reaction formulas are speculated below:

$$Ga_2O_3 + C_3N_4 \rightarrow 2GaN + 3CO + N_2$$



$$3V_2O_5 + 5C_3N_4 \rightarrow 6VN + 15CO + 7N_2$$

Since the products, in particular, the nitrides and N_2, are all thermodynamically stable, the above reactions can propagate to completion according to the SSM principles.[12] The possible reason AlN cannot be formed from Al_2O_3 might be that Al_2O_3 is very stable and the carbon-rich species cannot first react with it at moderate temperatures. On the other hand, in our experiments, the reaction of In_2O_3 with a-$C_3N_{3.69}$ only leads to metal In instead of InN in the final products. Therefore, we can conclude that either process can be the controlling step to the overall reaction.

To summarize, a new route for preparing nitrides GaN and VN is reported here. The reaction pathway involves a two-step process by using the as-synthesized a-$C_3N_{3.69}$ as precursor. The route is so potent that a series of nitrides can be directly synthesized from their oxides at moderate temperatures. A striking feature of this novel method is that a-$C_3N_{3.69}$ serves as both the carbothermal reduction agent and the nitridizing agent.

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Supporting Information Available: SEM images of the GaN and VN powder samples, XRD pattern of the VN product, EDX analysis of GaN and VN powder products. This material is available free of charge via the Internet at http://pubs.acs.org.

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