Notes

An Alternative Synthesis of Cyclotrigallazane, $[H_2GaNH_2]_3$, a Precursor to Nanocrystalline, Phase-Inhomogeneous Gallium Nitride, GaN

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In search for advantageous single-source precursors to the broad-band semiconductor gallium nitride, GaN, we have turned our attention to developing suitable group 13−15 systems containing none or a minimum number of organic ligands but having, preferably, hydrogen and/or halides. Some excess of reactive nitrogen ligands versus the ideal 1:1 nitrogen to gallium stoichiometry should also be beneficial by virtue of suppressing product enrichment in gallium from redox or deamination side reactions. For example, compounds such as gallium azide,[1] organo azides,[1a,b,2a−e] bis(diorganylamine) azides,[2f] and organohydrazides[2e,g,h] were utilized mostly in GaN film-forming CVD processes.

One of the advantageous precursors to GaN that fulfills some of these criteria is gallazane, $\{H_2GaNH_2\}$. It was first reported by Storr[3] as a benzene-insoluble, polymeric solid, $[H_2GaNH_2]_n$, obtained from a stoichiometric reaction between $H_3Ga{\bullet}NMe_3$ and NH_3 via facile dihydrogen elimination. Gladfelter and co-workers[4] later reinvestigated this reaction and found that, in fact, it resulted in the molecular cyclotrigallazane, $[H_2GaNH_2]_3$. This precursor upon pyrolysis yielded the new and rare cubic/hexagonal layers of gallium nitride, which were thought to constitute a topochemically induced and kinetically favored nanocrystalline variety of GaN. The exact crystallographic description of this seemingly phase-inhomogeneous material is subject to ongoing scrutiny and further investigations.[4c] However, the synthetic circumstances which led to the novel GaN phase(s) raise questions about other possible routes to this material.

We recently reported on two simple approaches to bulk nanocrystalline GaN powders.[5−7] First, we utilized the metathetical nitriding system, $GaBr_3/Li_3N$, in hydrocarbon/diglyme solvents, that resulted in precursors which were pyrolytically converted to hexagonal GaN materials.[6] Interestingly, the same reactant system under autoclave conditions (benzene solution, 280 °C) was described to give an apparent physical mixture of the hexagonal and cubic phases of GaN.[8] Second, we synthesized a new gallium imide, $\{Ga(NH)_{3/2}\}_n$, from the transamination/deamination reactions of $[Ga(NMe_2)_3]_2$ with liquid or gaseous NH_3.[7] This very advantageous precursor contains only residual organic ligands but has an excess of reactive nitrogen and upon a final deamination step is converted to light colored, nanocrystalline GaN materials. These solids were found by XRD and TEM to be the cubic/hexagonal variety as originally demonstrated by Gladfelter and co-workers. Similarly, an experimentally less convenient direct pyrolysis of $[Ga(NMe_2)_3]_2$ under flow of NH_3 gave materials which, in our case, were interpreted as the phase-inhomogeneous, cubic/hexagonal GaN (as above)[7] but, in a parallel report,[9] were instead claimed to be cubic GaN with stacking faults. Clearly, additional data are needed to shed more light onto possible pathways to these phase-inhomogeneous materials as well as on factors that are behind their structural details.

The original syntheses of gallazane utilized $H_3Ga{\bullet}NMe_3$ and NH_3 (gas or liquid phase).[3,4] We report herein a related but much simpler reaction system, $LiGaH_4/NH_4X$ (X = Cl, Br), in diethyl ether solution, that accomplishes the same synthetic goal (eq 1). A similar reaction system in Et_2O, $LiAlH_4/NH_4X$ (X = Cl, Br), was successfully utilized for the preparation of the iminoalane precursor, $[HAlNH]_n$, in one of the most simple precursor routes to high purity AlN.[10] In that case, the preferred combination included X = Br since the precursor was insoluble in Et_2O and the ether-soluble LiBr could be conveniently separated from it. The most obvious advantage of our system compared with the original one stems from the use of the readily available ammonium salts as the source of nitrogen in place of ammonia. Also, the use of $LiGaH_4$ instead of $H_3Ga{\bullet}NMe_3$ improves the overall process efficiency by eliminating one synthetic step ($H_3Ga{\bullet}NMe_3$[11a] is made from $LiGaH_4$[11b] in about 60−70% yield). However, both $LiGaH_4$ and $H_3Ga{\bullet}NMe_3$ are only moderately stable at ambient temperatures and all subsequent preparations should be carried out immediately using the freshly isolated materials. Regarding the $LiGaH_4$, we found this compound to be soluble in the mother-ether solution, which remained clear for a few days if stored at −30 °C. On the other hand, the compound quickly turned gray following the removal

$$3LiGaH_4 + 3NH_4X \xrightarrow[0\ ^\circ C]{Et_2O} [H_2GaNH_2]_3 + 3LiX + 6H_2 \quad (1)$$

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of Et_2O. This isolated gray material could not be completely redissolved in fresh ether and formed gray slurries.

On the basis of the reported insolubility of the gallazane, we first performed the reaction for X = Br[12] with the hope to easily separate the product from ether-soluble LiBr. The amount of the evolved H_2 was within 2% of the expected from eq 1, but surprisingly, the major product was soluble in the mother liquor. This *in situ* soluble product was shown to be the cyclotrigallazane (in admixture with LiBr and some NH_4Br), on the basis of the IR characterization for the freshly isolated, briefly evacuated solid and by comparison with a pure sample obtained from a parallel reaction for X = Cl (*vide infra*). It was later found from the IR and NMR studies that the gallazane was gradually decomposing in the course of days with the evolution of H_2 and NH_3 and precipitation of a gray solid. This solid upon isolation and evacuation was shown by IR to be polymeric. A similar polymeric product was obtained if the volatiles were removed from the filtered and clear solution, the solid residue was evacuated for several hours (it turned gray) and then redissolved in fresh Et_2O and filtered, and the grayish filtercake was evacuated again and characterized. The IR bands[13] at 3200 and 1509 cm^{-1} were consistent with the presence of mostly −N(H)− groups, and the band at 1900 cm^{-1} could result from the −Ga(H)− groups in the solid. If some of a briefly pumped (0.5 h) polymeric solid was placed in an evacuated flask with an attached trap cooled to −196 °C, the collected gases were found by IR and vacuum line techniques to contain a small amount of a noncondensable, H_2, and condensables, Et_2O (residual) and NH_3. It was clear that both the cyclotrigallazane and the polymeric solid derived from it were still undergoing slow changes with the evolution of H_2 and NH_3. Especially, the detection of NH_3 indicated deamination, $\{>GaNH_2\} + \{H_2NGa<\} = \{>GaN(H)Ga<\} + NH_3$, and, as a consequence, the enrichment of the polymeric product in gallium.

For example, a sample of a product was prepared from two cycles consisting of the removal of volatiles, 2 h evacuation, redissolution in fresh Et_2O, filtration, etc., which should separate the quite soluble LiBr from the less soluble products and promote only a moderate condensation of the cyclotrigallazane (as elucidated above). The IR spectrum for this solid showed the characteristic sharp bands of cyclotrigallazane (*vide infra*) superimposed on the broad bands typical of the polymeric product. The elemental analysis for this solid[14] was close to that expected for the cyclotrigallazane but was somewhat deficient in H and N relative to Ga, in agreement with the observed evolution of H_2 and NH_3. Although the studies in the system X = Br provided a general understanding of the reactions and led to the isolation of the products, the system's utility was hampered by a tedious and inefficient separation of LiBr from the products.[15]

The successful, high-yield synthesis of the cyclotrigallazane was accomplished for X = Cl, i.e. from the combination of $LiGaH_4$ and NH_4Cl in Et_2O solution.[16] The reaction followed the anticipated course (eq 1), and the precipitation of ether-insoluble LiCl provided a convenient means of its separation from the product. Additionally, the overall performance of the system was improved by using the ether-soluble $LiGaH_4$ *in situ* as well as the filtration of solids, mainly unreacted NH_4Cl, at early stages of the reaction. The elemental analysis confirmed the gallazane composition of the product. In the original communication on the synthesis of cyclotrigallazane,[4a] only a few characteristic IR bands were reported, possibly due to partial overlap with the bands of the *n*-undecane mull. Thus, our data provided the first full IR spectrum for the compound. In this regard, the originally quoted bands matched well with our spectrum. We also attempted a ^1H NMR study in toluene-d_8 for a range of samples from all preparations of the compound. We consistently found two broad resonances at δ 4.45 and −0.33 of weak intensities that integrated 1:1 and which were tentatively assigned to the Ga*H* and N*H* hydrogens in the cyclotrigallazane, respectively. Interestingly, for samples run several hours to days past preparation, an additional sharp peak at δ 4.51 appeared that grew with time at the expense of the resonances at δ 4.45 and −0.33. This peak has been attributed to dissolved dihydrogen[17] and was consistent with the evolution of H_2 as discussed above.

In our hands, perhaps the most surprising properties of the cyclotrigallazane were its good *in situ* solubility in Et_2O and its thermal frailty at ambient conditions. Thus, upon isolation, the compound was found to appreciably decompose with the evolution of H_2 and NH_3. This was confirmed by analyzing the volatiles formed over the evacuated compound in an experiment similar to the one described earlier. The resulting product was polymeric and not soluble in Et_2O. The exact nature of the polymeric derivative is not known at this point. The evolution of dihydrogen and ammonia and the IR characterizations[12,13] could suggest rather facile elimination−condensation, $\{H_2GaNH_2\} = \{-(H)GaN(H)-\} + H_2$, and deamination, $\{>GaNH_2\} + \{H_2NGa<\} = \{>GaN(H)Ga<\} + NH_3$. However, a participating reductive elimination of dihydrogen from

(12) A sample of $LiGaH_4$, 0.30 g or 3.72 mmol, was suspended in 30 mL of Et_2O, and 0.36 g or 3.72 mmol of NH_4Br in 30 mL of Et_2O was prepared in another flask. The whole system was thoroughly degassed by freeze−thaw cycles. The NH_4Br slurry was slowly added at 0 °C to the solution of $LiGaH_4$ resulting in gas evolution. The mixture was stirred at rt (room temperature) overnight, and the noncondensable gas, H_2, was measured on a calibrated vacuum line, 7.56 mmol (expected 7.44 mmol). After several days at rt, the products consisted of some insoluble grayish solid, Et_2O-soluble gallazane and LiBr, and unreacted NH_4Br. The evacuated insoluble solid was shown by IR to be a mixture of a polymeric material and unreacted NH_4Br. IR (KBr, cm^{-1}): 3200 (s, br), 1931 (s, br), 1614 (w), 1510 (w), 1400 (w) 1295 (m), 991 (m, br), 733 (s), 671 (s), 560 (br, s). The characterization of the isolated cyclotrigallazane matched ref 16 (*vide infra*).

(13) IR (KBr, cm^{-1}): 3200 (s, br), 1900 (s, br), 1609 (vw), 1509 (w), 1401 (vw), 1293 (w, br), 1154 (vw), 972 (m, br), 709 (m), 540 (s, br).

(14) Anal. Found (calcd) for $H_{12}Ga_3N_3$: H, 3.80 (4.59); Ga, 78.53 (79.45); N, 14.99 (15.96); C, 0.89 (0); Li, 0.11 (0); Σ98.32; Ga/N = 1.05/1.00; H/(Ga + N) = 1.73.

(15) The pyrolyses of these products resulted in GaN materials which by elemental analysis were shown to have significant lithium and bromine contents.

(16) Typically, $LiGaH_4$ was prepared on a 10 mmol scale[11b] and the clear, ethereal solution containing the compound was used *in situ*. To this solution, a sample of 0.54 g or 10 mmol of powdery NH_4Cl was slowly added at 0 °C resulting in a vigorous gas evolution and precipitation of a white, finely suspended solid (presumably LiCl). The mixture was stirred at rt for 4 to 6 h and filtered. The clear solution containing the cyclotrigallazane was stable at rt for at least 2 days and longer if stored at −30 °C. Data for freshly isolated, shortly evacuated samples of cyclotrigallazane are as follows. IR (KBr, cm^{-1}): 3311 (w), 3299 (m), 3245 (m), 1889 (s), 1870 (s), 1833 (s), 1524 (m), 1509 (w), 979 (m), 952 (s), 710 (s), 679 (m), 649 (s), 535 (s), 510 (s). Anal. Found (calcd) for $H_{12}Ga_3N_3$: H, 4.36 (4.59); Ga, 79.73 (79.45); N, 15.72 (15.96); C, <0.3 (0); Li, 0 (0); Σ99.81; Ga/N = 1.02/1.00; H/(Ga + N) = 1.91/1.00. ^1H NMR (toluene-d_8): δ 4.45 (Ga*H*, 2H; $\nu_{1/2}$ = 90 Hz), −0.33 (N*H*, 2H; $\nu_{1/2}$ = 33 Hz). MS [*m*/*e* (intensity) (ion)]: peak clusters around 262 (100) ($[H_2GaNH_2]_3$ − H or M − H), 245 (59) (M − NH_2 − 2H), 190 (74) (M − GaH_2 − 2H), 173 (67) ($\{H_2GaNH_2\}_2$ − 3H or M* − 3H), 158 (17) (M* − NH_2 − 2H), 86 (4) ($\{H_2GaNH_2\}$ − H, 71 (7) (GaH_2; also, contribution from atomic Ga).

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the $-GaH_2$ moieties, a known decomposition pathway for gallanes, could not be ruled out.

For pyrolysis toward GaN, the thermal instability and resulting material's enrichment in gallium were rather disadvantageous and suggested processing steps that minimized their extent. Preliminary pyrolysis studies were performed for both solids, cyclotrigallazane and polymeric material, which were freshly prepared and appropriately evacuated. The experimental variables included the use of NH_3 or vacuum, temperatures from 300 to 600 °C, and times from 2 to 5 h. The resulting materials were gray to dark gray nanocrystalline GaN that, generally, were shown by XRD to be the cubic/hexagonal variety reported by Gladfelter and co-workers but displayed a wider range of phase inhomogeneity.[18]

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