3512 *J. Am. Chem. Soc.* **1998,** *120,* 3512−3513

Detonations of Gallium Azides: A Simple Route to Hexagonal GaN Nanocrystals

Alissa C. Frank,[†] Frank Stowasser,[†] Harald Sussek,[†]
Hans Pritzkow,[†] Claudio R. Miskys,[‡] Oliver Ambacher,[‡]
Michael Giersig,[§] and Roland A. Fischer*,[†]

Anorganisch-chemisches Institut
Universität Heidelberg, Im Neuenheimer Feld 503
D-69120 Heidelberg, Germany
Walter-Schottky-Institut
Technische Universität München, Am Coulombwall 14
D-85748 Garching, Germany
Hahn-Meitner-Institut, Glienickerstrasse 100
D-14109 Berlin, Germany

Received November 10, 1997

The recent development of commercial blue-light emitters based on gallium nitride (GaN) has propelled these materials into the mainstream of interest. GaN combines high chemical inertness, radiation resistance, and the capability of working at elevated temperatures with high quantum efficiency.[1] However, unlike other important compound semiconductors, e.g., CdSe and InP,[2] a simple and reliable chemical route to colloids of group 13 nitride quantum dots is still to be developed. The synthesis of high-quality nanocrystals generally requires a fast nucleation, a rapid termination of the growth, and effective thermal annealing of the particles. This is very difficult to achieve for GaN.[3] Even the reaction of Ga with a N_2/NH_3 mixture induced by a dc arc plasma only yields comparably large crystallites with a broad size distribution of 20−200 nm.[4] Here, we demonstrate a new method for the synthesis of nanocrystalline GaN by the controlled detonation of suitable gallium azides, thus taking advantage of the unique properties of covalent azides.[5,6] Detonations closely resemble the conditions of an arc discharge, characterized by GPa pressures (shock waves) and very high local temperatures acting on a microsecond time scale.[7]

The monomeric, low-melting, and soluble trialkylamine adducts $(R_3N)Ga(N_3)_3$ ($R_3N = Et_3N$, Me_3N, $Me_2N{-}C_nH_{2n+1}$, $n = 8{-}16$) are quantitatively obtained as white solids from $Na[Ga(N_3)_4]$ (**1**) and the respective amine in toluene in solution.[8] The molecular structures of **1** and **2** are shown in Figure 1. Complex **1** is a coordination polymer with a heptacoordinated Na center.[9]

Gallium azides exhibit a complex association chemistry in the condensed phase. At elevated temperatures, the gradual elimination of N_2 from the azide units builds up a GaN framework (TGA/XRD studies).[10] This may be considered as a formal analogy to the condensation process in sol−gel chemistry. Shock heating terminates the crystallite growth by detonation of the sample.

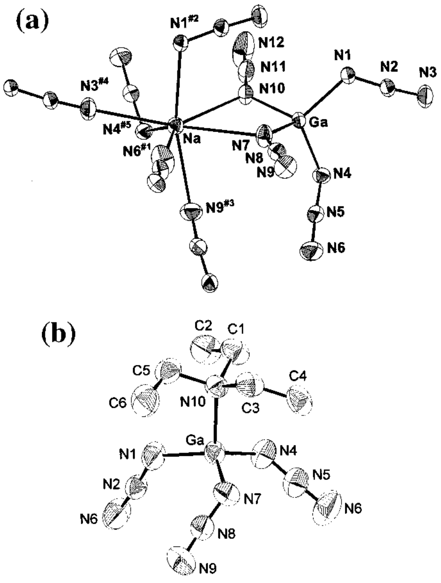
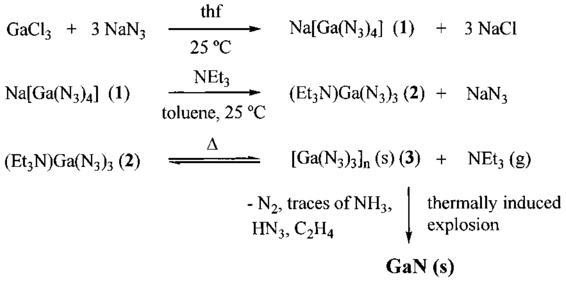


Figure 1. (a) Representative part of the molecular structure of polymeric $Na[Ga(N_3)_4]$ (**1**) in the solid state. (b) Molecular structure of $Et_3NGa(N_3)_3$ (**2**) in the solid state.

Scheme 1



A detonation of molten $(Et_3N)Ga(N_3)_3$ (mp = 43 °C) in a sealed 71 mL stainless steel pressure vessel equipped with a pressure gauge (350 bar; Parr instruments, 4740 bomb) under inert gas (N_2) was induced by rapid heating (30 °C/min) to 400 °C. After the observation of a sudden pressure rise from 1 to 10−200 bar (depending on the amount of starting material), indicating the detonation, the vessel was immediately cooled to room temperature. Nanocrystalline GaN was collected as a very voluminous gray powder. Samples of different particle size were obtained simply and reproducibly by the variation of two parameters: the total amount of the precursor and the “condensation” time at 150 °C.[11] The molecular precursor $(Et_3N)Ga(N_3)_3$ is in equilibrium with its highly associated coordination polymer $[Ga(N_3)_3]_n$ (**3**) and the free base NEt_3 (see above). Base-free triazidogallium is extremely explosive.

[†] Universität Heidelberg.

[‡] Technische Universität München.

[§] Hahn-Meitner-Institut.

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(9) Crystal data for **1**: $N_{12}GaNa$, $M_w = 260.83$, orthorhombic, $P2_12_12_1$, $a = 7.011(4)$ Å, $b = 9.666(5)$ Å, $c = 12.320(6)$ Å, $V = 834.9(8)$ Å^3, $\rho = 2.075$ mg/m^{-3}; $Z = 4$, $\mu = 3.33$ mm^{-1}, number of reflections used = 2107 ($R_{int} = 0.0000$) (2107 unique measured), $R = 0.0275$, $R_w = 0.0683$, R3m/V diffractometer, graphite monochromator, Mo Kα = 0.710 73 Å. Detailed discussion of the structure will be published elsewhere. Data for **2**: $C_6H_{15}N_{10}Ga$, $M_w = 296.99$, monoclinic, $P2_1/n$, $a = 8.394(5)$ Å, $b = 13.059(8)$ Å, $c = 11.939(7)$ Å, $\beta = 95.93(5)°$, $V = 1301(2)$ Å^3, $\rho = 1.515$ mg/m^{-3}; $Z = 4$, $\mu = 2.11$ mm^{-1}, number of reflections used = 4905 ($R_{int} = 0.0000$) (4906 unique measured), $R = 0.0326$, $R_w = 0.0784$, R3m/V diffractometer, graphite monochromator, Mo Kα = 0.710 73 Å. The methylene carbon atoms of the triethylamino group are disordered over two positions (0.78, 0.22).

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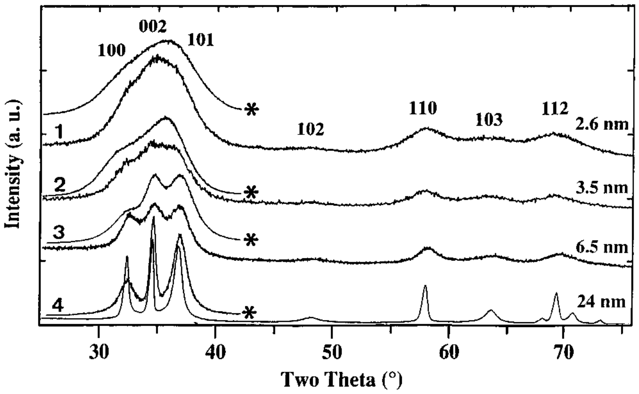

Figure 2. X-ray powder diffraction (XRD) patterns of samples #**1**−#**4** and Rietveld simulations (marked with an asterisk). XRD patterns were recorded on a Siemens D-500 X-ray diffractometer with Cu Kα1,2 radiation ($\lambda_{K\alpha1}$ = 1.540 59 Å, $\lambda_{K\alpha2}$ = 1.544 43 Å). The peaks are anisotropically broadened. Additional experiments using tablets of powder samples prepared at 1.2 kbar pressure resulted in an intensity reduction of the 002 reflection, compared to reflections 100 and 101. It can be concluded that the crystallites have a platelet-like shape perpendicular to [102]. Pressure forces the plates to orientate vertical to the *c* axes.

Ex situ analysis of the exhaust fumes by GC-MS and NMR revealed the presence of C_2H_4, HN_3, and NH_3, giving evidence that the protecting ligand NEt_3 has partially been attacked.[12] The GaN particles are thus embedded into a C/H/N matrix, which was removed by tempering (600 °C, N_2 (1 atm), 12 h or 450 °C, O_2 (1 atm),[13] 30 min), giving white fluffy powders. IR spectroscopy proved the absence of hydrocarbon impurities. Elemental analysis[11] and SEM-EDX showed a ratio Ga/N = 1.0.

X-ray powder diffraction (XRD) patterns of samples #**1**−**4** were indexed as pure hexagonal-phase GaN (Figure 2). The average particle size was estimated from the Scherrer formula.[14] Rietveld simulations allowed the assignment of the crystallites' shapes.[15,16]

Transmission electron microscopy (TEM) and electron diffraction give evidence for hexagonal GaN nanocrystallites of 2−3(±1)nm (#**1**), 3−4(±1)nm (#**2**), 6−7(±2)nm (#**3**; Figure 3), and 24(±3)nm (#**4**). Raman spectra of sample #**4** exhibit the A_1(LO) phonon mode at 735 cm^{-1}. The symmetry and position of the peak are indicative for strain-relaxed GaN.[17] At 566 cm^{-1}, the typical GaN E2 lattice vibration is observed by Raman as well as by IR spectroscopy.[18]

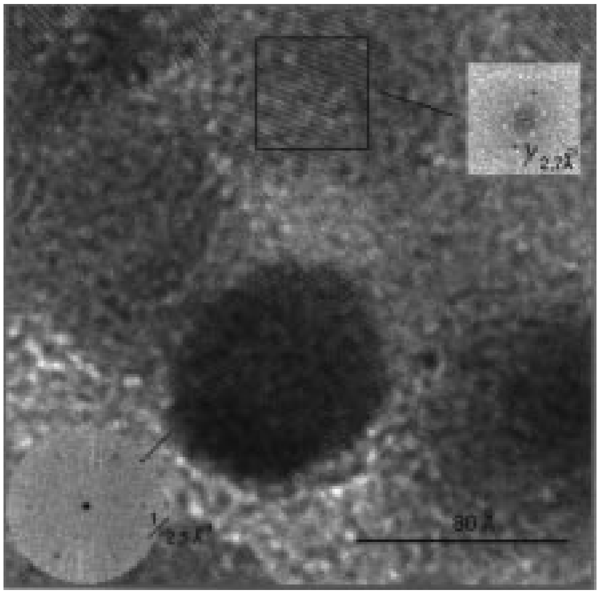

Figure 3. High-resolution transmission electron micrograph of sample #**3**. Images were taken on a Philips CM-12 transmission electron microscope, equipped with a supertwin lens. Two representative crystals are depicted, viewed down different crystallographic axes. The diffraction patterns and plane spacings obtained are characteristic for hexagonal (wurtzite) GaN.

The photoluminescence spectra of the material exhibit a low-energy emission at 2.2 eV which is a characteristic feature of GaN.[19] A high-energy emission was observed for the first time in chemically prepared nanocrystalline GaN samples. It is blue-shifted up to 4.2 eV (band edge luminescence of bulk GaN at 300 K, 3.45 eV) with decreasing particle size and decreasing temperature.

Nanodisperse GaN crystallites with particle sizes of 1−2 nm embedded into a sodium matrix were also obtained by detonation of the tetrazide **1**. This compares nicely with the report by Yamane et al. on the synthesis of large GaN microcrystals by the solid-state reaction of Ga metal with sodium azide.[20] The nanodispersity of our material is a consequence of our special conditions, of course. It is possible to avoid the detonations described here and to pyrolyze precursors of type **2** in solvents such as trioctylphosphine oxide (TOPO) above 350 °C in the course of several days. However, the crystallinity of the obtained nanoparticles is very poor (less effective annealing!) and the organic matrix (black tar due to decomposition of the solvent) could not be removed completely.

We suggest that explosivity, commonly considered as a compound's most undesired, troublesome, and dangerous property, may offer interesting opportunities for nanochemistry. Since a full range of molecular precursors quite similar to $(Et_3N)Ga(N_3)_3$ are available as well for Al and In, the method may well be extended to AlGaN and InGaN particles and can be optimized further, for example, by the applied stabilizing Lewis base.[21]

Acknowledgment. This work was supported by the Alfried Krupp Award for Young University Teachers (R.A.F.).

Supporting Information Available: Rietveld simulations of XRD powder patterns of samples #**1**−**4**, description of the experimental setup, Raman spectra of sample #**4**, photoluminescence spectra at 5 and 300 K of samples #**2** and #**3**, atomic coordinates, thermal parameters, bond distances and bond angles for **1** and **2** (53 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA9738438

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(11) For 6.5 nm particles (#**3**): a sample of 1.65 g (5.6 mmol) $(Et_3N)Ga(N_3)_3$ was kept at 150 °C for 10 min followed by thermally induced detonation (final pressure 15 bar; yield 95%). Anal. Found (calcd) for #**3**: Ga 82.91 (83.27); N, 16.36 (16.73); O, 0.42 (0.0); C, 0.20 (0.0); H, 0.11 (0.0). For 24 nm particles (#**4**): a sample of 1.65 g (5.6 mmol) $(Et_3N)Ga(N_3)_3$ was kept at 150 °C for 60 min followed by thermally induced detonation (final pressure 15 bar; yield 92%). Particle sizes above 1 μm were achieved by detonating a sample of 4.0 g (13.5 mmol) $(Et_3N)Ga(N_3)_3$. The sample was kept at 150 °C for 10 min before the thermally induced detonation (final pressure 40 bar; yield 92%). The Scherrer formula allows for the determination of particle sizes up to 1 μm.

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