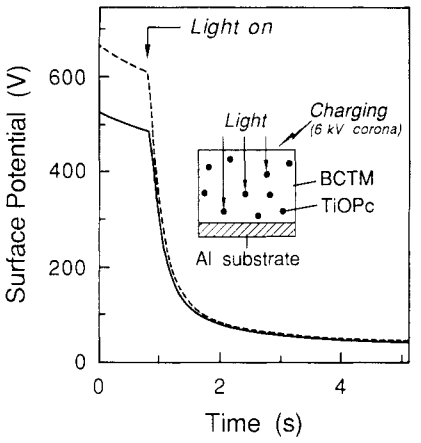

Figure 3. Photoinduced surface potential decay curves by the continuous irradiation of 630-nm light (3.15 μW cm^{-2}) for the photoreceptor with 0.5 wt % TiOPc pigment embedded in a BCTM (30 wt % MBDQ and 20 wt % PDA in polycarbonate): (—) positive charging; (---) negative charging. The optical density of the 17-μm photoreceptor was 0.51 in 630 nm (λ_{max} of TiOPc).

obtained for bipolar-charge-transporting organic materials. It should be noted in Figure 2 that the hole and electron mobilities of the present bipolar charge transport system are equal (within experimental error) to those of the films doped with only PDA or MBDQ separately. This finding clearly demonstrates that PDA and MBDQ function independently and do not interfere with each other in this system. Thus, it is emphasized that the present system provides a model for the material design of BCTMs.

In our laboratory, studies on the following two applications based on BCTMs are in progress: electroluminescent and electrophotographic devices. If fluorescent compounds that can capture both electrons and holes (i.e., recombine holes and electrons) are embedded in BCTMs, the resulting composite thin films may function as an electroluminescent device. On the other hand, if colored compounds that can separate the charges (i.e., generate holes and electrons) by light absorption are embedded, the resulting films may function as an electrophotographic photoreceptor that can work equally in both cases of positive and negative charging. An example of the latter is shown in Figure 3. The photoreceptor was prepared by embedding particles of titanylphthalocyanine (TiOPc) pigment as a charge-separation agent in the present bipolar charge-transport active matrix. As expected, its photoinduced discharge rates were quite independent of the polarity of charging. The electrophotographic properties of this novel type of photoreceptors will be presented in a forthcoming paper.

Cyclotrigallazane, $[H_2GaNH_2]_3$. Its Preparation, Structure, and Conversion to Cubic Gallium Nitride at 150 °C

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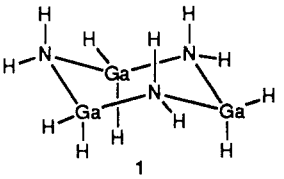
As a III–V semiconductor having a bandgap of 3.5 eV,[1] there is interest in using gallium nitride in various optoelectronic devices. The known syntheses of bulk powders of GaN involve reactions of various gallium sources (Ga_2O_3,[2] Ga,[3] or $[NH_4]_3[GaF_6]$[4]) with ammonia conducted at high temperatures (>900 °C) and result exclusively in gallium nitride having a wurtzite (hexagonal) structure. Reports of epitaxial thin films of cubic gallium nitride grown by molecular beam epitaxy or organometallic vapor-phase epitaxy on substrates such as GaAs,[5] MgO,[6] or cubic SiC[7] have appeared. In this paper we describe the synthesis and structure of the novel trimer cyclotrigallazane and its reaction to give the first bulk samples of cubic GaN.

The only previous report of the reaction between $(Me_3N)GaH_3$ and NH_3 suggested the uncharacterized product was polymeric.[8] In our hands H_2GaNH_2 was prepared in 75% yield simply by passing gaseous NH_3 over solid $(Me_3N)GaH_3$[9] at room temperature for 1 h. The less-than-quantitative yield results from losses of the volatile gallane starting material, and higher yields can be achieved by condensing liquid ammonia directly on $(Me_3N)GaH_3$. Even without further purification, elemental analysis of the white powder indicated the formula H_2GaNH_2, and the lack of measurable carbon confirmed the quantitative displacement of trimethylamine.[10] The highest mass peak observed by using EI mass spectrometry (20-eV ionizing voltage) was 262 amu, corresponding to the parent ion of the trimer minus one hydrogen. The extremely limited solubility of cyclotrigallazane in all common organic solvents precluded us from obtaining a ^1H NMR spectrum. The infrared spectrum of the powder dispersed in *n*-undecane reveals ν_{N-H} vibrations at 3297 and 3247 cm^{-1} and ν_{Ga-H} vibrations at 1890, 1865, and 1832 cm^{-1}. Careful sublimation at 40–50 °C and 0.05 Torr yielded a small number of clear, colorless crystals that were shown by single-crystal X-ray crystallography to consist of a six-membered rings in a chair conformation, **1**,[11] similar to that observed in $[H_2BNH_2]_3$.[12]



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Thermogravimetric analysis of cyclotrigallazane shows an abrupt weight loss (4.5%) at 150 °C followed by a

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(10) Anal. Calcd: Ga, 79.45; N, 15.96; H, 4.59; C, 0.00. Found: Ga, 79.70; N, 15.71; H, 4.46; C, 0.08 (Analitische Laboratorien in Engelskirchen, West Germany).
(11) X-ray crystallographic data: monoclinic crystal system, $P2_1/m$ space group, a = 8.079 (8) Å, b = 8.506 (9) Å, c = 8.079 (8) Å, β = 138.24 (5)°, Z = 2, V = 370 (1) Å^3, T = −90 °C, $R(F)$ = 0.119 $R(wF)$ = 0.118. Twinning of all crystals examined resulted in higher values of $R(F)$ and $R(wF)$. Full details of the structural solution are available in the supplementary material and will be reported separately. Structural data: Ga(1)–N(2) = 1.96 (2) Å, Ga(1)–N(2′) = 1.96 (2) Å, Ga(3)–N(2) = 1.98 (2) Å, Ga(3)–N(4) = 1.96 (1) Å; N(2)–Ga(1)–N(2′) = 100 (1)°, N(2)–Ga(3)–N(4) = 99.6 (9)°, Ga(1)–N(2)–Ga(3) = 117.0 (8)°, Ga(3)–N(4)–Ga(3′) = 118 (1)°.
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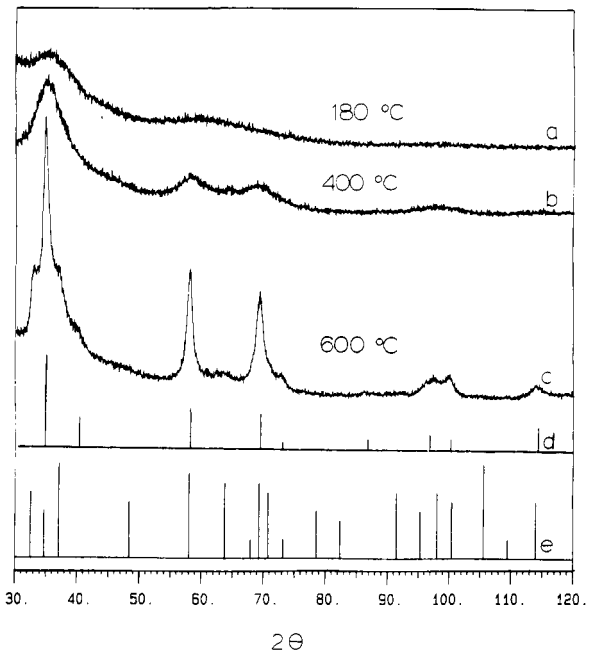

Figure 1. X-ray powder diffraction results. Patterns a–c were obtained on powders heated for 4 h at the specified temperature under argon. Patterns d and e are the calculated diffraction pattern for cubic GaN and the experimental pattern for hexagonal GaN, respectively.

smaller, more gradual weight loss (1.7%) between 210 and 500 °C. Mass spectrometric studies indicated that hydrogen was the only product evolved at temperatures greater than 200 °C, but that hydrogen, ammonia, and some gallium were detected during the initial weight loss. Due to the involatility of elemental Ga, its appearance in the mass spectrum indicates the occurrence of a small amount of sublimation of starting material. The precipitous loss of hydrogen from cyclotrigallazane may be facilitated by its crystal structure in which the nearest intermolecular contact to each hydride ligand is a nitrogen-bound proton. During the overall conversion, the white starting material is transformed to a dark gray solid. Figure 1 illustrates the X-ray powder diffraction patterns obtained after treating three separate samples of cyclotrigallazane for 4 h under argon at the specified temperatures. Surprisingly, the onset of crystallinity is evident even in the sample treated at 180 °C. Figure 1 also includes a graphical representation of the known diffraction pattern for hexagonal GaN. The notable absence in our patterns of several reflections of *h*-GaN,[13] coupled with the similarity to the patterns of GaP and other cubic (sphalerite) structures,[14] suggested that we had formed cubic GaN. The elemental analyses suggest[15] that the cubic phase may be nonstoichiometric having the formula $GaN_{0.83}$, a value that corresponds closely to the overall weight loss observed in the TGA experiments. Our calculated powder diffraction pattern for cubic GaN (a = 4.50 (2) Å) agrees well with the experimental results. The lattice constants of the various thin films of cubic GaN range from 4.52 to 4.55 Å.[5-7] The cubic GaN was found to convert to the hexagonal phase; however, the phase transition is slow. After 120 h at 900 °C under Ar, the transition is approximately 50% complete.

(13) Powder Diffraction File, International Center for Diffraction Data, Swarthmore, PA, card no. 2-1078.
(14) Powder Diffraction File, International Center for Diffraction Data, Swarthmore, PA, card no. 32-397.
(15) Anal. Calcd for $GaN_{1.00}$: Ga, 83.27; N, 16.73. Found: Ga, 85.99; N, 14.31; H, < 0.5; C, < 0.5 (Galbraith Laboratories).

Why the cubic phase of GaN should form remains unexplained. On one hand this GaN synthesis is conducted at temperatures well below those typically used, perhaps in a temperature range where the cubic phase is thermodynamically favored. Alternatively the synthesis may well lead to a kinetically trapped, metastable phase. Experiments addressing this fundamental issue are in progress.

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Supplementary Material Available: Description of the structural solution, tables of atomic positional and thermal parameters and crystallographic data, and an ORTEP drawing of the molecule (7 pages); a list of the structure factors (4 pages). Ordering information is given on any current masthead page.

Ferrocene Polymers with "Polyaniline" Backbones

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Transiton-metal complex polymer modified electrodes have become an area of intense research activity as practical applications may exist for these unique polymers.[1] Polymers containing ferrocene covalently bonded to the polymer[2] or immobilized within a host polymer matrix[3] have been used for practical applications and fundamental studies. Polymer films of poly(vinylferrocene) often are used in these studies. Recent reports have appeared in which pyrrole units have been appended to one or both of the cyclopentadienyl rings.[4,5] Synthetically, attaching the pyrrole to the cyclopentadienyl ring(s) can be difficult, and good-quality polymers generally result when the mo-

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