Low-Temperature OMCVD of InN Thin Films from the Novel Air-Stable Single-Molecule Precursor Azido{bis[(3-dimethylamino)propyl]}indium, $(N_3)In[(CH_2)_3NMe_2]_2$

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Introduction

The group III nitrides EN (E = Al, Ga, In) and their ternary alloys $E^{(1)}_{1-x}E^{(2)}_{x}N$ are promising materials for light-emitting diodes and semiconductor lasers operating at short wavelengths of the optical spectrum.[1] Thin films of EN have been grown by several methods including hydride vapor-phase epitaxy (HVPE), electron cyclotron resonance assisted molecular beam epitaxy (ECR-MBE),[2] and organometallic chemical vapor deposition (OMCVD) using mixtures of ER_3 and ammonia (NH_3) at substrate temperatures above 950 °C (for AlN and GaN) and extremely high V:III gas-phase ratios (e.g., >1000:1).[3] However, the release of N_2 from the growing EN film is a general problem. Intrinsic defects, in particular N vacancies, may lead to n-type materials, which are difficult to p-dope controllably.[4]

The OMCVD of InN or In containing ternary alloys is a rather challenging problem, because of the low-lying onset of decomposition at $T \geq 550$ °C,[5] ranging below the minimum temperature for efficient thermal activation of ammonia,[6] the most common nitrogen source for EN growth (N−H bond strength 3.9 eV). In certain cases the bulk concentration of In is lowered by the formation of In droplets on the surface.[7] For these reasons only few reports exist on the growth of InN using organometallic precursors and ammonia.[8] In addition, a high amount of hydrogen atoms (10^{20} cm^{-3}) is generally incorporated into the nitride films in conventional OMCVD processes, which is believed to compensate the p-doping Mg for GaN.[9] The search for alternative sources for N or the group III component, or so-called single-source precursors, which contain both indium and nitrogen in one molecule, has thus largely been motivated by lowering the deposition temperatures, growth in the absence of ammonia or other hydrogen sources, simplifying the handling of the precursors, the process control, and the problems with the disposal of the NH_3 exhaust. For Al and Ga such low-temperature single-source precursors have been designed on the basis of volatile group III amide, azide, and hydrazide compounds and have been investigated in OMCVD studies.[10] This is different for InN. To our knowledge, there is only one single report in the literature on a single-molecule source to InN. The solid-state pyrolysis of polymeric $[In(NH_2)_3]_\infty$ was studied.[11] We report here on the first example of an *air-stable*, *nonpyrophoric*, and *volatile* single-source precursor for *low-temperature* OMCVD of crystalline InN.

Experimental Section

All manipulations with organometallic compounds were conducted using a drybox, carefully dried solvents (≤1 ppm H_2O, by Karl−Fischer titration), a good ventilated hood, and inert-gas (N_2) techniques (Schlenk-line).

Synthesis of 1. $BrIn[(CH_2)_3NMe_2]_2$[12] was treated with an equimolar amount of $Tl[PF_6]$ in CH_2Cl_2 for 5 h. After filtration an excess of dried NaN_3 was added to the solution of $[PF_6]\{In[(CH_2)_3NMe_2]_2\}$, and the mixture was heated to reflux

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for 24 h. Product **1** was obtained as analytically pure colorless crystals after filtration and removal of the solvent, sublimation at 50 °C (10^{-3} Torr dynamic vacuum), and crystallization from CH_2Cl_2/*n*-pentane at −35 °C. Analytical data for **1**: mp 64 °C; IR (CH_2Cl_2 solution, CaF_2 plates) $\nu(N_3)$ 2058 vs, 1462 s. Elemental anal. calcd for $C_{10}H_{24}InN_5$: C, 36.49; H, 7.35; N, 21.28. Found: C, 36.02; H, 7.21; N, 20.70 (trace impurities: Br ≤ 0.1; F ≤ 0.04). ^1H NMR (399.78 MHz, toluene-d_8, 25 °C) 2.19 (t, 2H, N−CH_2), 2.14 (s, 6H, N−CH_3), 1.70 (quin, 2H, −CH_2−), 0.47 (t, 2H, In−CH_2). ^{13}C NMR (100.53 MHz, toluene-d_8, 25 °C) 61.4 (N−CH$_2$), 43.9 (N−CH$_3$), 22.8 (−CH$_2$−), 5.7 (In−CH$_2$).

OMCVD Experiments. The reactor[13] was kept at 500 °C at a basic pressure of 10^{-6} Torr for 5 h (loaded with the cleaned substrates). Then the precursor reservoir was filled with 0.50 g of **1** under inert-gas atmosphere and cooled to −30 °C. The system was pumped down again to 10^{-6} Torr for 1−2 h. During this time the substrates were heated to 100−150 °C above the deposition temperature for 30 min (to liberate any condensed material). When GaAs substrates were used, the reactor was never heated above 500 °C. After this the temperature of the oven was allowed to stabilize at the desired value (350−570 °C). The temperature of the bubbler was then adjusted to 70 °C, allowing **1** to sublime through the hot zone of the reactor at pressures of 0.5×10^{-4} to 2.0×10^{-4} Torr. In the case of carrier gases and flow conditions, the temperature of the bubbler was kept at 90 °C at a pressure of 7.5×10^{-1} Torr at typical flow rates of 50 sccm (N_2) and 5−10 sccm (NH_3). The MBE grown AlN buffer layers of 50 nm on Al_2O_3 were provided by O. Ambacher and H. Angerer. The GaN buffer layer of 1.5 μm were OMCVD grown according to ref 10a.

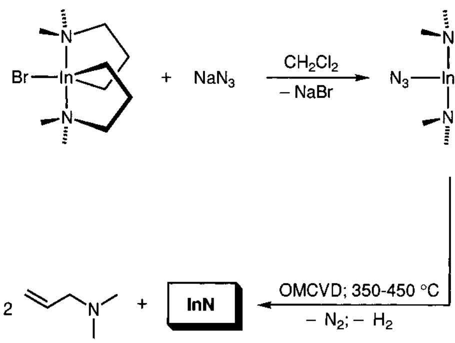
Structural Characterization. X-ray diffraction measurements were performed on a Philips PW3040 diffractometer including a PW3020 $\omega-2\theta$ two circle diffractometer equipped with the thin-film package and a graphite monochromator. Cu Kα radiation was used. The instrumental resolution in $\theta-2\theta$ mode is about 0.1° in 2θ and in the X-ray rocking curve mode about 0.15° in (ω). The samples were mounted on a single-crystal sample holder to improve the signal-to-noise ratio. All samples were analyzed by a conventional $\theta-2\theta$ scan (JCPDS-ICDD No. 2-1450).

Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Analysis (EDS). The samples were examined using a JEOL JSM-35C scanning electron microscope equipped with an EG&G Ortec System 5000 X-ray analyzer system (insensitive for C, N, O) and a Hitachi S-3200N instrument with a Oxford LINK ISIS energy-dispersive X-ray analyzer (detection limits for C, N, and O about 0.5−1 atom %).

Results and Discussion

Precursor Synthesis and InN Thin-Film Deposition. The prototype of a new class of alternative InN-sources is the intramolecularly adduct stabilized organoindium azide, azido{bis[(3-dimethylamino)propyl]}-indium, $(N_3)In[(CH_2)_3NMe_2]_2$ (**1**), which is readily obtained as colorless low melting crystals from $BrIn[(CH_2)_3NMe_2]_2$ (**2**) and sodium azide in quantitative yield (Scheme 1). It melts at 64 °C, sublimes at 50 °C (10^{-3} Torr, dynamic vacuum), and is monomeric in the gas phase (CI-MS). Generally, covalent metal azides tend to be explosive.[14] But **1** did not detonate when treated under various conditions, including sudden heating or exposure to a mechanical shock. Compound **1** is much more stable, far less explosive, and thus considerably safer in handling than hydrazine or common azide compounds (N_2H_4, HN_3, EtN_3, Me_3SiN_3), which are in discussion as alternative N sources for group III nitride growth.[6] Similarly to related intramolecularly adduct stabilized organo gallium azides,[10a,b] the increased stability of **1** may be attributed to the coordinative shielding of the In center by the aminopropyl group.

Scheme 1



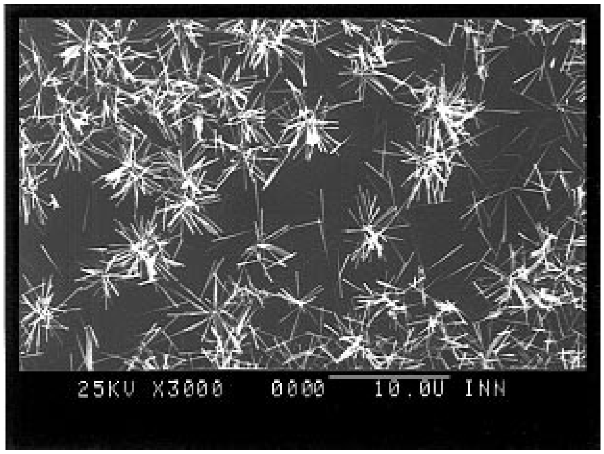


Figure 1. SEM image of InN whiskers grown from **1** on (0001) sapphire (400 °C, 0.1 mTorr; 1 μm/h).

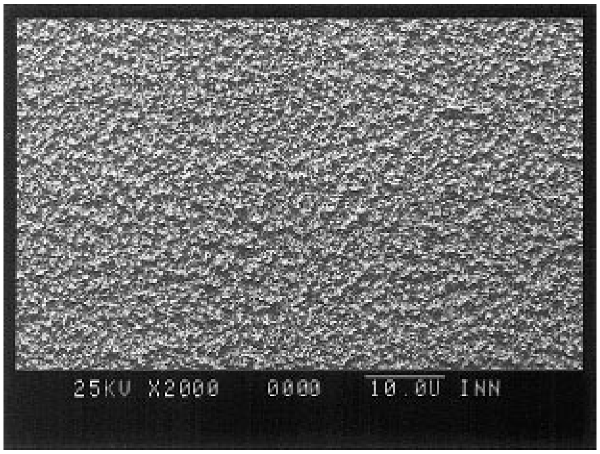


Figure 2. SEM image of a representative InN film grown from **1** on a 500 Å buffer layer on sapphire (450 °C, 0.2 mTorr; 5 μm/h).

Using **1** as precursor we have deposited InN films on (111) silicon, (001) GaAs, and (0001) Al_2O_3 (sapphire, also with AlN and GaN buffer layers) substrates under various low-pressure OMCVD conditions either without any carrier gas in vacuo or using a mixture of N_2 and NH_3 as carrier gases (Figures 1−3). A simple horizontal isothermal hot-wall tube reactor[13] was used at temperatures from 300 to 500 °C. After typical periods of 1−2 h, almost transparent films with a brownish to gray luster were obtained. The growth rates (by profilom-

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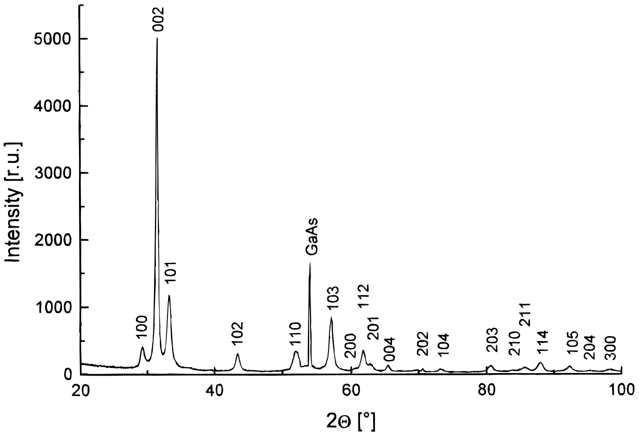

Figure 3. XRD pattern of a InN film grown from **1** on (001) GaAs (420 °C, 0.15 mTorr; 3 μm/h). All reflections were indexed. Reflections arising from In and In_2O_3 are absent (reflections due to the GaAs substrate are marked).

etry) were between 0.3 μm/h (best crystallographic properties) and 5 μm/h (homogeneous, very smooth surface, polycrystalline or amorphous nature).

Exhaust Gas Analysis and Precursor Fragmentation. The condensable fractions of the exhaust gases were analyzed by means of ^1H and ^{13}C NMR spectroscopy. The main products were unsaturated amines, e.g., $H_2C{=}CHCH_2NMe_2$ (≥95 mol % by GC-MS). From this it is conclusive that the nitrogen atom of the chelate ring of **1** serves not as the (major) N source for the InN growth but rather as stabilizing Lewis donor ("spectator ligand") to complete the coordination sphere of the indium center. The advantageous fragmentation properties of the chelating 3-(dimethylamino)propyl group during OMCVD processes has already been demonstrated previously.[13] It cleaves from the In center via β-elimination to form of $H_2C{=}CHCH_2NMe_2$ and isomers of this.

Structural Characterization and Composition. A quite interesting InN whisker growth was observed for films deposited directly on (0001) sapphire at substrate temperatures between 450 and 500 °C and vacuum conditions (Figure 1). This nucleation problem can be solved by predepositing a polycrystalline buffer layer of 500 Å of AlN (MBE grown) or 1 μm of GaN (OMCVD grown). Then, smooth, homogeneous, and crystalline InN layers were obtained at temperatures as low as 350 °C (Figure 2). X-ray diffraction studies on representative samples revealed the common hexagonal wurzite phase of InN and the preferred orientation of the (0002) direction of the InN crystallites parallel to the (0001) direction of single-crystalline sapphire substrate. Crystalline hexagonal InN films were grown on (001) GaAs also (Figure 3). The calculated lattice parameters $a_0 = 3.536$ and $c_0 = 5.698$ agree nicely with the JCPDS data of $a_0 = 3.53$ and $c_0 = 5.69$. The literature values for the c_0/a_0 relation for polycrystalline samples are in the range of 1.615 ± 0.008 (our results: $c_0/a_0 = 1.611$). In addition, the level of important impurities such as elemental indium and indium oxides (In_2O_3) as well as carbon was estimated from the EDS data (signals for In and N only; C, O, and Br not detected) to be below a 1 atom %. It is therefore reasonable to conclude that In:N ~ 1.0, with certainly not more than about 1 atom % of N deficiency. The characterization of the films by photoluminescence spectroscopy (PL) was not possible. This is probably due to the polycrystalline nature of the samples (large amount of grain boundaries) and because **1** was of "analytical purity" (≤99 mol %) only. When traces of $BrIn[(CH_2)_3NMe_2]_2$ (**2**) (~1−2 mol %; Br 0.3−0.5 wt %, by elemental analysis) were present elemental indium was detected by XRD. When traces of O_2 and/or H_2O were present (leaking, impure NH_3), the characteristic diffraction pattern of the In_2O_3 phase was detected. The InN films may still contain some amounts of other impurities (e.g., Si, Cl, Li, Al, etc.) introduced by the chemical synthesis of **1** but not noticed by means of EDS and XPS (detection limits ~ 0.5 atom %). A synthesis of **1**, based on electronic grade starting compounds and other high-purity reagents, in addition to much cleaner (H_2O- and O_2-free) deposition conditions to improve the quality of the grown InN films in terms of the optical properties (PL), certainly warrants further investigations.

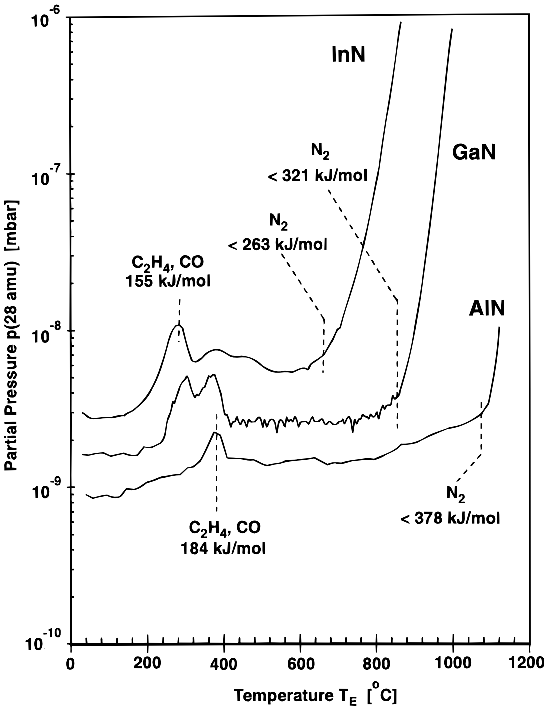

Figure 4. Thermal stability of EN films in vacuo. Temperature-programmed gas effusion of N_2 (28 amu, linear ramp with 20 °C/min) from the InN film of Figure 2 (data for OMCVD grown GaN and AlN are included for comparison).

Role of Ammonia. It is known from other work[15] that ammonia can be beneficial to achieve single-crystalline growth of EN materials when single-source precursors related to **1**, such as $[Et_2Ga(N_3)]_3$, are used. This effect was attributed to a lack of surface mobility of the oligomeric precursor fragments ("$[GaN]_3$"). But in our case, the fragmentation of the *monomeric* InN precursor is likely to produce small fragments which may have a reasonably good surface mobility. Our data indicate, that ammonia is not a crucial co-reactant to grow crystalline InN from **1**. In fact, the best results were obtained *without* ammonia (Figures 2 and 3). Interestingly, **1** does not react easily with ammonia (melt, 100 °C, 1 atm of NH_3), while $[Et_2Ga(N_3)]_3$ gives

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$[Et_2Ga(\mu\text{-}NH_2)(\mu\text{: }\eta^1\text{-}N_3)GaEt_2]$ under similar conditions, for example.[16]

Thermal Stability of the Films. The InN films were also characterized by temperature-programmed gas effusion experiments in an UHV chamber, equipped with a quadrupolar mass spectrometer.[17] Figure 4 shows the temperature dependence of the partial pressure of the specific mass $m/z = 28$ (N_2) effusing from the film. The onset of the InN decomposition at 684 °C nicely fits to literature data (energy of activation 253 kJ mol^{-1}, exponential increase of N_2 partial pressure).[4] The small low-temperature peak (300 °C) is assigned to CO or C_2H_4 on the basis of comparison with other EN samples.[18] The diagram nicely illustrates the use of a *low-temperature single-molecule precursor* for InN growth. The nitridic In−N bonds of the crystalline solid-state phase are incorporated in the growing layer by fragmentation of the azidic In−N_3 moiety into In−N and N_2. A considerably large "thermal window" of 300 °C between the minimum temperature for the deposition of InN from **1** at 350 °C and the traditional conditions of 650 °C can now be used.

Summary. We have shown that a new type of nitrogen-rich single-source precursor for low-temperature OMCVD of InN can be derived by intramolecular base adduct stabilization.[19] InN growth is possible in the absence of ammonia. The handling of this novel precursor to obtain crystalline films is much easier and probably safer than that of the binary systems InR_3/NH_3. It may, for example, be an interesting alternative precursor for the formation of InGaN alloys by CBE or OMCVD.

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