

# Towards complex Group III(13)-pnictide nanopowders and their applications

Jerzy F. Janik\*

*AGH University of Science and Technology, Faculty of Fuels and Energy, Al. Mickiewicza 30, 30-059 Kraków, Poland*

Received 20 May 2004; received in revised form 18 January 2005; accepted 20 January 2005

Available online 13 April 2005

Dedicated to Professor Robert T. Paine—a great teacher, scientist, and man—on the occasion of his 60th birthday. Sto lat!

## Abstract

A review is presented of selected precursor systems leading to bulk powders—often in the nanosize range—made mostly of Group III(13)–V(15) elements (pnictides, i.e., nitrides, phosphides, and arsenides). Both single-source precursor and precursor solution mixture approaches are shown to derive a range of unique composites and doped nanopowders for potential applications in modern electronics, ceramics, and gas adsorption/storage/separation processes. Especially, a range of GaN-based materials that include the composites of GaN/AlN and GaN/TiN as well as of Mn-doped GaN (GaMnN) can be produced. Prospects for the utilization of such powders are posed by, among others, underlining a need for further powder processing by compacting/sintering methods toward mechanically stable and manageable pellets, slides, and other shapes. The compacted material forms of the powders could be considered as relatively inexpensive and valuable precursor materials for a range of applications such as GaN and GaN-modified alternative substrates for heterostructures in optoelectronics and spintronics.

© 2005 Elsevier B.V. All rights reserved.

*Keywords:* III–V; Nanocomposites; Nanopowders; Nitrides; Gallium nitride GaN; Phosphides; Arsenides; Pnictide

## 1. Introduction

It has been a thrilling professional experience in the last couple of decades to participate in the molecular chemical research ventures that have impacted the emergence and growth of the new interdisciplinary field called inorganic-metallic materials chemistry [1]. Advances in this new field, in turn, are powering the rapid emergence of nanotechnology as an economic engine. During that time, even in inorganic synthetic chemistry, the boundaries between organometallic, main-group, and transition metal coordination chemistry have become blurred and indistinguishable. Nonetheless, the goal of the enterprise remained—to design and prepare

suitable precursor systems that upon pyrolysis could be converted to new material compositions and/or new material forms [2]. At the same time, the synthetic chemist was now expected to tailor the material's properties, characterize it properly with unfamiliar techniques, and perhaps do parametric process development studies, etc. One reward for taking on this added technical challenge is the realization of truly unique, unanticipated materials that frequently possess nano-dimensional features and functionalities both by design and unintentionally. The molecular level synthetic changes in numerous precursor systems go to completion at lower temperatures than encountered in classical materials manufacturing processes so that temperature promoted crystallizations can be much better controlled on smaller dimensional scales. Another reward is that specially designed precursors may lead to materials forms and morphologies otherwise unattainable such as fibers, tubes, films, spherical powders, QD colloids,

\* Tel.: +48 12 617 2577; fax: +48 12 617 2066.

*E-mail address:* [janikj@uci.agh.edu.pl](mailto:janikj@uci.agh.edu.pl).

high surface area/low density inorganic sorbents, catalyst supports, etc.

In the area of III(13)–V(15) materials, perhaps the most evident examples of the progress in utilization of precursor chemistry include the development of nitride heterostructures via chemical deposition processes (CVD) [3]. However, in GaN-based structures in order to achieve the target layer conductivities the nitride lattice must be modified with dopants such as Mg or Si. The needs for detailed structural characterization and in-depth understanding of mixed-center and/or defected lattice stabilities for such complex systems cannot be overstressed.

Given the considerable progress in the development of thin film nitride-based devices from CVD chemistry, one may question the needs and prospects for the so-called bulk powder syntheses of nitride materials. In this regard, one can rest assured that well-founded knowledge acquired from III–V nanopowders is critical to the continued development of new compositions, new material forms, and even to new layered nanostructures. Also, size-homogeneous, well characterized nanoparticles made or dispersed in a supporting medium, if reproducibly available, find wide utility in applications requiring quantum dot (QD) or other size-dependent compound properties [4]. Unfortunately, reproducible bulk nanopowder syntheses are difficult, and recently we have mostly been faced with unfulfilled claims about the potential of III–V bulk nanopowders with no apparent applications in sight, especially, in the field of electronics. On the ceramics side, most notably, hexagonal boron nitride h-BN, a relatively inexpensive and commercially available powder material has been prepared in large quantities as a nanopowder with spherical particle morphology as well as in platelet form [5].

We have recently been engaged in exploring an exciting new potential for nanopowders of Group III-nitrides by way of compacting them into mechanically stable pellets. For example, high pressure/high temperature processing of pure nanopowders of GaN has produced translucent compacts of this type. Compacted forms made of pure or mixed element stoichiometries may provide a reliable route to affordable optoelectronic substrates, especially, in those cases where appropriately large single-crystals with suitable characteristics are very difficult and/or expensive to manufacture.

Herein are summarized relevant aspects of several studies on the synthesis of complex Group III–V bulk nanopowders that often extend beyond all nitride-based systems to include phosphides and arsenides. The pathways described below are unconventional in comparison to traditional powder mixing of crystalline, coarse-grained components followed by “homogenization”. Such treatments are inadequate and were excluded as means to reach the goal. The methodology employed here has the powerful benefit that it ensures molecular level mixing and homogeneity throughout the sample as long as intergranular growth, diffusion, and phase separation are suppressed. In addition, an anaerobic process provides oxygen-free powders at relatively low temperatures. In contrast, traditional approaches that rely on less expensive oxygen derivatives of Group III elements may offer less control over crystallite sizes (higher temperatures required) and yield materials with residual oxygen content. From the point of view of processing the powders toward compact forms, the trade-offs we make by selecting one of the two approaches over the other are not obvious and a careful consideration in each particular case is required.

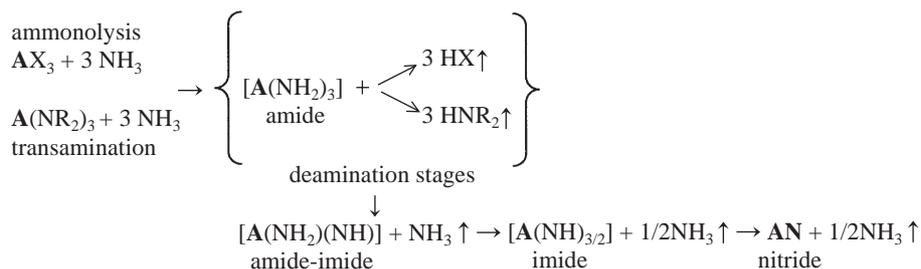
## 2. Single-source precursor routes

The concept behind single-source precursor routes to solid state materials involves the use of compounds that, upon thermal treatment, undergo efficient elimination–condensation reactions resulting in formation of the target solid material [4c,6]. For example, an A(III)B(III) product may be obtained from a thermally promoted, stepwise elimination–condensation process such as shown in the following idealized sequence:



where XY, composed of the reactant substituent fragments, should preferably be a volatile compound that ensures its easy removal from the reaction system. In addition, XY should be inert to secondary reactions, and sufficiently stable to pyrolytic decomposition at temperatures of the process. In most cases the detailed mechanisms for the stepwise elimination–condensation reactions involved in solid state materials production are poorly understood. In fact, in most systems, it has not even been determined whether the elementary steps are intramolecular or intermolecular in nature.

Another important pathway, especially in the area of A(III)-nitrides involves thermally driven transamination (or ammonolysis)/deamination chemistry such as shown in a simplified manner in the scheme:



In each reaction step, intermediate product and gaseous by-product can, in principle, be isolated and identified. Further, the isolated and purified intermediates can be subsequently processed toward the binary powder materials. The intermediates, shown in square brackets, can be, depending on the system, ring, cage or oligomeric molecular compounds or polymeric solids. The latter are especially found for final stages of processes wherein the elimination–condensation reactions take place under unfavorable conditions of diffusion controlled solid-state decomposition. In many examples, it is in this stage that the purity of final products is determined since competing elimination chemistry/pyrolytic decomposition of any remaining X and/or Y substituents (first scheme) or R/X substituents (second scheme) or other high-temperature specific reaction pathways can prevail leading to retention of residuals. However, this is also a stage that offers some potential for fabricating composite materials. Indeed, solution mixing of soluble precursors or soluble intermediates from the early reaction stages can provide complex compositions through pyrolysis of molecularly scrambled solid assemblages obtained upon removal of solvent. Some promising systems of this kind, that the author was involved in studying, are described below. It is noted that in many of the systems described here no in-depth parametric studies to optimize materials properties were done. Thus, the results are intended to outline major reactivity trends in the systems. It is also the author's opinion that the unpredictable complexity of the discussed reaction systems represents quite a typical picture of decomposition behavior of many other single-source precursors, especially, pyrolyzed as bulk powders.

### 2.1. $\text{Al}[\text{Si}(\text{CH}_3)_3]_3/\text{NH}_3$ system toward nano-AlN/SiC [7]

This system was initially devised as a molecular precursor route to aluminum nitride, AlN. Given the much weaker Al–Si bond energy compared to Al–C bond energies in aluminum alkyl compounds, it was expected that progressive elimination of  $\text{HSi}(\text{CH}_3)_3$  (dehydrosilylation) from a presumed silyl aluminum–ammonia complex, and subsequent condensation of the coordinatively unsaturated Al–N fragments, might take place under less demanding conditions than found with the known  $\text{AlR}_3/\text{NH}_3$  elimination–condensation reactions. Two molecular compounds,  $\{[(\text{CH}_3)_3\text{Si}]_2\text{Al–NH}_2\}_2$  and  $\{[(\text{CH}_3)_3\text{Si}]_2\text{Al}(\text{NH}_2)_2\}_3\text{Al}$ , were isolated from the reactions of the silyl aluminum reagent and ammonia. In addition, an insoluble, poorly characterized polymeric solid was obtained. Pyrolysis of each of the three precursors at 930 °C, under vacuum, gave a single nanocrystalline product with a hexagonal lattice. In all cases,  $\text{HSi}(\text{CH}_3)_3$  was evolved as the major gaseous by-product; however, methane also formed already at 300 °C and dihydrogen appeared at 600 °C. The appearance of methane and dihydrogen is consistent with parallel thermal decomposition of the  $-\text{Si}(\text{CH}_3)_3$  groups and likely retention of silicon in the final ceramic products. After pyrolysis at 930 °C, the product from the decomposition of  $\{[(\text{CH}_3)_3\text{Si}]_2\text{Al–NH}_2\}_2$  was characterized as a solid solution of nanocrystalline AlN and SiC with an atomic Al to Si ratio approx. 2 to 1 and a wurtzite structure. For a similar pyrolysis of  $\{[(\text{CH}_3)_3\text{Si}]_2\text{Al}(\text{NH}_2)_2\}_3\text{Al}$ , the product was a solid solution of AlN and SiC with an Al to Si ratio of approx. 5 to 1 and a wurtzite structure. It is interesting to note that the results point to a possibility of preparing these complex systems in a wide range of compositions. The use of a single precursor already containing Al–N and Si–C bonds, therefore, offers a unique opportunity to reach the solid solutions at relatively low temperatures.

### 2.2. $\text{Al}[\text{Si}(\text{CH}_3)_3]_3/\text{PH}_3$ system toward nano-AlP/SiC [8]

This reaction system could ideally lead to pure AlP upon complete elimination of  $\text{HSi}(\text{CH}_3)_3$  according to a similar elimination pathway proposed for  $\text{Al}[\text{Si}(\text{CH}_3)_3]_3/\text{NH}_3$ . However, in this case, no molecular compounds could be isolated at room temperature. By utilizing an excess of  $\text{PH}_3$  and long reaction times, a poorly characterized polymeric solid

precursor was obtained. The pyrolysis of the solid at 900 °C, under vacuum, resulted in a blue–black product that, by powder XRD, was a mixture of cubic AlP and hexagonal SiC. A semi quantitative X-ray elemental analysis showed the Al to Si atomic ratio of about 4 to 1. These composites are essentially composed of a robust and relatively unreactive SiC component and an oxidation/hydrolysis sensitive (PH<sub>3</sub> evolution), “ceramically diluted” AlP component. Such solid materials could be envisioned for use as convenient sources of phosphine which could be released upon hydrolysis at ambient conditions.

### 2.3. $X_3Ga \cdot P[Si(CH_3)_3]_3$ ( $X=Cl, Br, I$ ) adducts toward nano-GaP/SiC [9]

In all cases, a 1:1 Lewis adduct was formed upon mixing solutions of a gallium halide with the silylated phosphine at room temperature. The solid adducts were isolated in quantitative yields and subjected, as pure compounds, to pyrolysis with the intent to form gallium phosphide, GaP, via stepwise eliminations of (CH<sub>3</sub>)<sub>3</sub>SiCl (dehalosilylation), another elimination–condensation pathway known for III–V compounds. Pyrolyses of the adducts were individually performed at 450 °C under vacuum affording in each case nanocrystalline GaP as the only crystalline component with average particle sizes varying between 4 and 5 nm. The intrinsic difficulty of completing the silane elimination chemistry resulted in retention of some carbon (for X=Cl, 4.5%; for X=Br, 0.7%; for X=I, 5.4%) and silicon (for X=I, 3.8%) in the products in the form of amorphous phases. Two points should be noted here. First, the elimination of (CH<sub>3</sub>)<sub>3</sub>SiCl is very efficient compared with the elimination of HSi(CH<sub>3</sub>)<sub>3</sub> from the aluminum systems described above. Second, there is a need for development of appropriate methods for the separation of crystalline III–Vs from amorphous Si/C phases formed at lower pyrolysis temperatures. At this stage, it seems that such products could only be used with difficulty as raw feedstock for gallium phosphide bulk powder syntheses.

In related extensive studies on the preparation of ternary III–V compound semiconductors, both mixed-pnictogen, e.g., GaAsP, GaInP, InAsP, and mixed-metal, e.g., GaInP, ternary nanopowders were shown to form by utilizing solution mixtures of appropriate three precursors from the pool of E[Si(CH<sub>3</sub>)<sub>3</sub>]<sub>3</sub> (E=P, As) and MX<sub>3</sub> (M=Ga, In; X=halide) [10].

### 2.4. $H_3Al \cdot N(CH_3)_3/E[Si(CH_3)_3]_3$ ( $E=P, As$ ) systems toward nano-AlP/SiC and AlAs/Al [11]

These reaction systems rely on HSi(CH<sub>3</sub>)<sub>3</sub> elimination chemistry and accompanying condensation of the Al–P and Al–As networks. It is instructive to point out that for E=P, the system can be considered structurally isomeric with the reaction system described in Section 2.2. In the present case, however, a high yield of the trimeric {H<sub>2</sub>AlP[Si(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>}<sub>3</sub> was isolated at room temperature, whereas no molecular species was produced in the former system. The precursor was pyrolyzed at 950 °C under vacuum affording nanocrystalline AlP, with an average crystallite size of 5 nm, as the only discernible crystalline phase. The elemental analysis showed Si and C contents of 11.3% and 4.6%, respectively. This corresponds to the ratio Si/C ~1. Similarly, a P/Al ratio of 1 suggests formation of a mixture of nanocrystalline AlP and amorphous SiC.

For the system with E=As, a room temperature stable, base-stabilized adduct {H<sub>2</sub>AlAs[Si(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>} · N(CH<sub>3</sub>)<sub>3</sub> was isolated. This adduct, upon pyrolysis at 450 °C under vacuum afforded a dark colored material that by powder XRD was determined to contain AlAs (2 nm ave. crystallite size) as the only crystalline component. However, the elemental analysis showed it to be significantly enriched in aluminum with an Al/As ratio ~1.8. In addition, small amounts of C, 0.4%, and Si, 1.8%, but no N were found.

Silane, HSi(CH<sub>3</sub>)<sub>3</sub>, elimination was not the only major reaction pathway in these systems. Ligand redistribution chemistry was found to compete at increased temperatures as evidenced by evolution of E[Si(CH<sub>3</sub>)<sub>3</sub>]<sub>3</sub> and dihydrogen. This was especially pronounced in the case of E=As leading to excess aluminum in the product. Interestingly, for E=P, the prevailing decomposition mechanism seemed to be the target silane elimination that lead to Al/P ratio corresponding to pure AlP while the accompanying thermal cracking of residual silane moieties resulted in some SiC retention. In this regard, reductive decomposition of H-alanes and H-gallanes accompanied by dihydrogen evolution and leading to elemental metals are commonly encountered and even utilized to make thin metal films [12].

### 2.5. $H_3Ga \cdot N(CH_3)_3/E[Si(CH_3)_3]_3$ ( $E=P, As$ ) systems toward nano-GaP/SiC and GaAs/Ga [13]

These systems are analogous to their aluminum counterparts listed above. Compared to the previously mentioned and related adducts, X<sub>3</sub>Ga · P[Si(CH<sub>3</sub>)<sub>3</sub>]<sub>3</sub>, they provide an advantageous halide-free environment.

The elimination–condensation chemistry is plagued here with similar side-reactions as described above (i.e., reductive decomposition of H-gallanes, thermal cracking of residual trimethylsilyl groups) resulting upon pyrolysis at 450–475 °C in complex nanocomposites containing, respectively, GaP/SiC and GaAs/Ga.

### 3. Utilization of molecular mixtures of precursors

As already mentioned, there is a significant potential in using precursors mixed on the molecular level as a source of intermediate molecular species for further processing to target III–Vs. This approach appears to have crucial advantages over related methods of making composite materials that employ traditional “simple” mixing of solid components and subsequent sinter/press/compact/ball mill processing to obtain homogenized, alas usually microsize composites. One would expect that, in favorable cases, by dissolving soluble precursors in an appropriate solvent, followed by solvent removal, the resultant solid mixture would provide homogeneously dispersed materials, i.e., solid solutions, doped binaries, or nanosize-scaled composites. This would be especially true for methods that employ precursor solutions in processing as, for instance, encountered in the aerosol-assisted vapor phase synthesis technique that has already been used to prepare pure boron nitride [5c] and gallium nitride [14] powders. The use of an appropriate precursor solution containing a modifying soluble component could, therefore, remedy many of the problems associated with homogenization aspects. However, the synergistic effect of such complex chemistry cannot be predicted up-front and complications may arise due to an increased number of chemical subsystems and accompanying kinetic pathways. In other words, no simple extrapolation can be applied to forecast an outcome of complex composite evolution as exemplified below. The recent very promising examples of such an approach are shown here to illustrate real advantages of such processing toward complex solid materials.

#### 3.1. $\{M[N(CH_3)_2]_3\}_2$ , $M=Al/Ga$ , system toward complex nanocomposites of AlN/GaN [15]

Since the individual metal amides of the type  $\{M[N(CH_3)_2]_3\}_2$ ,  $M=Al$  or  $Ga$ , were shown in separate studies [15,16] to yield upon transamination/deamination treatment the respective nanocrystalline nitrides, an Al/Ga=1/1 mixture of the metal amides was employed as a mixed precursor system in order to obtain molecularly mixed composites AlN/GaN or solid solutions AlGaN. The pyrolysis studies were preceded by investigations of equilibria taking place both in hexane and toluene solutions of the two starting metal amides. Complex time-dependent equilibria were observed, and the solutions contained the mixed bimetallic dimer  $\{M[N(CH_3)_2]_3\}_2$ ,  $M=Al/Ga=1/1$  (up to approx. 50%) and individual metal dimers. Upon removal of the solvent, samples of the solid mixture were heated at 700, 900, and 1100 °C under a flow of ammonia, and nanocrystalline bimetallic nitride products were obtained. At least some of these nitrides were shown to be complex mixtures of the individual metal nitrides, AlN and GaN, and their solid solution,

AlGaN. Such an outcome is consistent with a correlation between the chemical nature of the initial bimetallic Al/Ga-amide-imide precursor (after transamination stage at RT) and the resulting composite compositions derived from them upon pyrolysis. These studies clearly pointed out potential complications in processing mixed precursors even from such apparently simple precursor sources as their homogenous solutions. However, the resulting nitrides' composites were unique in their chemical make-up offering an unparalleled set of potential properties for further applications, for instance, in their compacted form. For example, high specificity and selective adsorption properties of many binary and complex Group III nitride powders support their use in gas storage and gas separation applications [5d,17].

#### 3.2. Aerosol-assisted [18] and anaerobic [19] syntheses of nanopowders of magnetic semiconductor GaMnN

The aerosol-assisted vapor phase synthesis of Group III-nitrides relies on the use of inexpensive, readily available, oxygen-bearing precursor solutions, e.g., salts such as nitrates, sulfates, acids, or alkoxy derivatives, to generate a mist of droplets that passes through a heated furnace in a stream of a nitriding gas ( $NH_3$ ). Powder is collected on an exit filter and is usually subjected to a follow-up treatment at increased temperatures under a flow of ammonia to complete nitridation reactions within the bulk of spherical particles made in the first stage (Fig. 1).

The specific spherical morphology and inexpensive initial precursors are perhaps the most obvious trademarks of the method while other advantages rest in the tailoring of such materials properties as surface area, density, and particle size. From the point of view of making complex materials, the method offers an opportunity to start with initial homogeneous solutions containing preset proportions of molecularly mixed precursors. In favorable cases, this provides increased opportunities for obtaining solid solutions, doped structures, kinetically controlled phases, and/or well mixed nanocomposites.

In the case of the system GaN/Mn, both aqueous and methanol solutions of precursors were used to generate aerosols (Fig. 2).

Both resulted in two different product morphologies. The final materials were shown to possess spheroid morphology and be composite mixtures of Mn-doped hexagonal lattices of GaN and cubic Mn(II)O. Mn-concentrations, estimated from magnetization measurements, were nearly the same for all the samples ( $x_{Mn} \sim 0.015$ ) regardless of the initial ratio of Ga/Mn. Acid leaching efficiently removed the MnO component leading to nanopowders of manganese-doped gallium nitride. Magnetization measurements (SQUID) and EPR studies revealed a range of magnetic centers. In this regard,  $Mn^{2+}$  centers with  $d^5$  electron configuration were most probably responsible for the observed paramagnetic behavior.

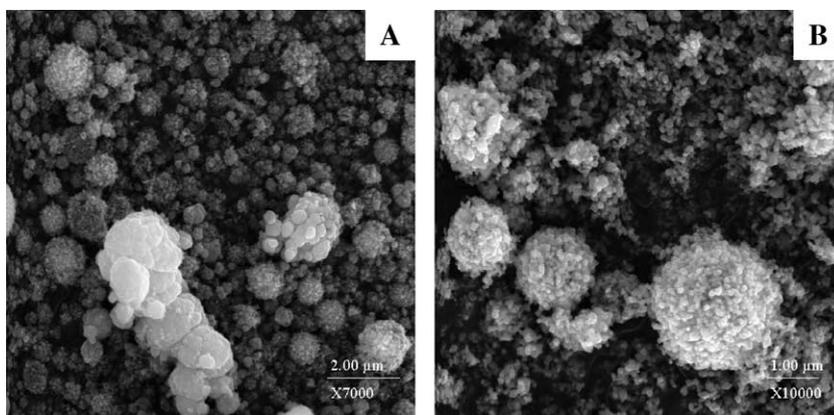


Fig. 1. SEM images for pure GaN prepared by aerosol-assisted synthesis from precursor methanol solutions: A—raw aerosol-generated powder and B—product after additional annealing at 1000 °C, NH<sub>3</sub> atmosphere. Note: (i) from EDX study, the bright shape-deformed agglomerates in A are carbons/soot from cracking of methanol; (ii) in B, GaN is prevalingly formed in this system as relatively large fine-grained spheres consisting of nanocrystallites.

Similar magnetic properties were observed for GaMnN grown by other methods. Small ferromagnetic and anti-ferromagnetic impurities were also present and the latter most likely corresponds to MnO.

The anaerobic approach for synthesis in the system GaN/Mn utilizes the gallium amide or gallium imide precursors, previously shown to yield pure nano-GaN [15,16] in combination with a suitable Mn-precursor. One of a selected manganese sources was manganese (III) acetylacetonate that was used in diethyl ether solutions/slurries with the gallium compounds and after suitable processing afforded gallium nitride hexagonal lattices doped with manganese. In these cases, the amounts of incorporated manganese centers were approximately twice as large as in the aerosol method, i.e., approx. 2.5% and 1.0–1.5%, respectively, as supported by EPR and SQUID measurements. Also, only small quantities of the Mn(II)O by-product, confirmed by magnetization measurements, were formed while this impurity was below detection limits by powder XRD. In another approach, a pre-formed nano-GaN powder was soaked in a solution containing the

manganese source followed by nitriding at increased temperatures in an attempt to modify the surface of nanograins. Powders with magnetically active Mn-centers were obtained proving that surface modifications of nanopowders constitute yet another way to reach GaN-based magnetic semiconductors.

The two precursor pathways, therefore, provide an extended range of GaN-based manganese-modified powders. Compacting/sintering of such powders is planned with hope to yield mechanically stable, applicable material forms for potential uses in spintronics.

### 3.3. Aerosol-assisted [20] and anaerobic [21] syntheses of nanopowders of composites in the system GaN/TiN

The aerosol-assisted process aimed at making GaN/TiN powder composites utilized a range of titanium-bearing compounds in aqueous and methanol solutions with gallium nitrate. The titanium sources included in situ made titanium (IV) nitrate and suitable solutions of titanium chloride, titanium isopropoxide, and titanium methoxide. After a

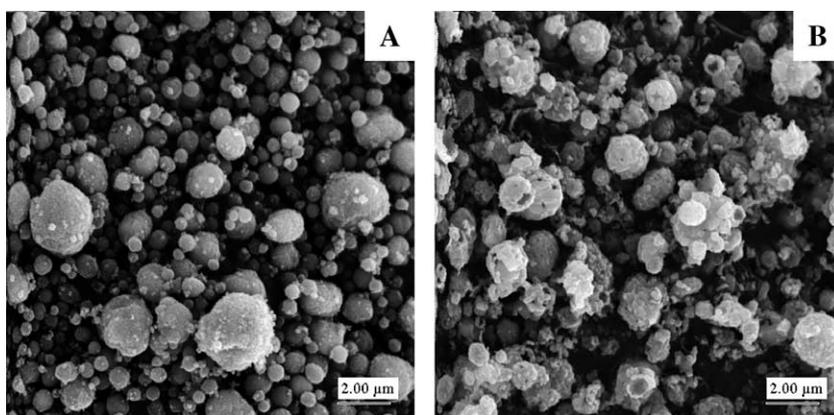


Fig. 2. Characteristic SEM images for composite systems GaN/Mn prepared by aerosol-assisted synthesis from aqueous precursor mixtures of gallium nitrate/manganese(II) nitrate: A—raw aerosol-generated powder and B—product after additional annealing at 1000 °C, NH<sub>3</sub> atmosphere. Note: (i) the product is found by XRD, EDX, and magnetization measurements to be a composite of nanocrystalline Mn-doped GaN and microcrystalline by-product MnO; (ii) after annealing, A vs. B, spherical morphology with abundant hollow particles is retained.

subsequent nitriding pyrolysis at 950–1000 °C, the initial aerosol powders afforded composite nitrides with the titanium component shown to contain some residual oxygen in a cubic solid solution phase “TiON” (Fig. 3).

Significant enrichment in titanium vs. starting atomic metal ratios was also observed, mostly due to sublimation of the h-GaN component and its partial decomposition at the highest pyrolysis temperatures. In this regard, mainly depending on the geometry of the crucible/oven set-up, droplets of gallium metal were occasionally seen on the bottom of the crucible which resulted from phase separation from the powder bulk. The aerosol synthesis provided the target composites, but with uncontrolled Ga/Ti ratios. The intrinsic problem in this system was the thermal instability of GaN at temperatures at and above 1000 °C. This temperature is necessary to make low-oxygen content GaN, but it is too low to complete nitridation reactions of any of the composite titanium precursors. The latter process was found, in a separate study, to proceed gradually at increased temperatures via cubicTiO and through the intermediate cubic “TiON” toward pure powders of TiN at 1200 °C under applied nitriding conditions [22].

In the anaerobic synthesis, composites of GaN and TiN were successfully made by processing solution mixtures of the metal amides  $\{M[N(CH_3)_2]_n\}$ ,  $M=Ga$ ,  $n=3$ ;  $M=Ti$ ,  $n=4$ . The overall process was reminiscent of the one used to make the composites AlN/GaN via the amide-imide solid precursor obtained from reactions of the metal amide mixtures with liquid ammonia [15]. The target composites, with crystallite sizes in the nanosize region, were formed in a range of pyrolysis temperatures from 600 °C to 1000 °C. At 1000 °C, some GaN decomposition took place as evidenced by formation of Ga–metal droplets. Therefore, the lack of metal–oxygen bonded species in the precursors and the efficient transamination/deamination reactions operating in this system supported oxygen-free composite formation in a wide temperature range generally lower than used in the aerosol synthesis. This also allowed for temperature-driven control of crystallite sizes of both components that ranged from a few to several tens of nanometers.

In the near future the GaN/TiN composites from both systems will be compacted to yield stable pellets. Such material forms could be used as relatively inexpensive substrates for growing free-standing GaN wafers [23]. They also might be employed to remedy problems associated with GaN/Ti contacts [24] or in other advanced applications in modern electronics that combine the semi-conducting properties of GaN and robust ceramic nature of TiN in the composites.

#### 4. Concluding remarks

In recent years, the synthetic chemist has faced expanding challenges related to the development of novel compositions and forms for advanced ceramic and electronic materials. Many of these challenges are related to (i) designing, making, and understanding more and more complex materials of controlled stoichiometries/structure and (ii) engaging in utilization of binary and complex nanopowders of this type.

The evidence presented here supports the premise that the bulk synthesis of III–V compositions, using either single-source precursors or molecular mixtures of precursors, offers a realistic approach for fabrication of unconventional nanocomposites, nanocrystalline solid solutions, and/or active-center doped nanocrystalline lattices. The intrinsic advantage of such processing is the control gained over crystallization in the nanosize region due to lower temperatures used to complete the elimination–condensation reactions compared to traditional processes. This enables formation of powders with a range of controlled morphologies and crystalline sizes including nanosize region, alas of a rather wide size distribution. Another important advantage derives from the ability to make unusual composite assemblages from temperature-driven condensation and crystallization processes occurring in the molecularly mixed starting systems (solid solutions, unstable kinetic phases, etc.). This, however, may have in certain cases a negative impact on materials quality if extremely pure materials are targeted

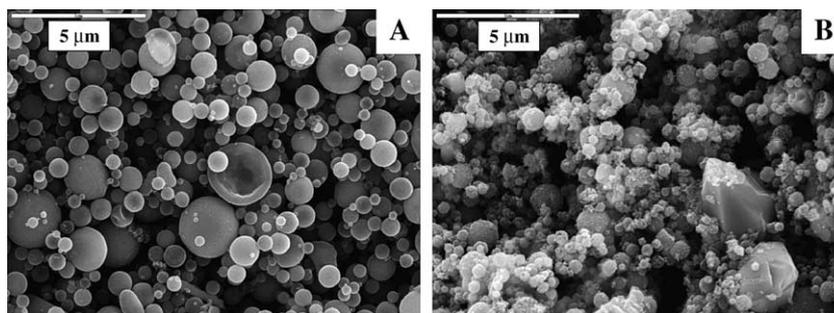


Fig. 3. Typical SEM images for composites GaN/TiN prepared by aerosol-assisted synthesis from aqueous precursor mixtures: A—raw aerosol-generated powder and B—product after additional annealing at 1000 °C,  $NH_3$  atmosphere. Note: (i) at least some of the smooth-surface spheres in A are hollow; (ii) in B, as supplemented by EDX and XRD measurements, GaN component is formed as large blocky crystallites while TiN retains spheroidal morphology of much smaller crystalline domains in the nanosize region.

because of the high probability of unintentional doping. Therefore, the urgent needs for development of target-specific ways to remove unwanted and chemically robust components from such solid mixtures should be emphasized.

The utilization of bulk III–V nanopowders is virgin with a notable exception of boron nitride. Digesting the wealth of knowledge accumulated in the last two decades, it is the author's strong opinion that there are worthwhile and realistic directions to be pursued, especially, for Group III nitrides. In this regard, the preliminary studies on pressing/sintering of some of the nanopowders into mechanically stable pellets are encouraging and suggesting such compacts could constitute relatively inexpensive and valuable precursor materials for a range of applications in modern electronics such as GaN and GaN-modified substrates for heterostructures in optoelectronics and spintronics.

### Acknowledgements

Support of Polish Committee for Scientific Research KBN Grant No. 3 T08D 043 26 is gratefully acknowledged.

Some of the discussed studies were part of the author's continuing involvement with the research groups of Prof. R.T. Paine (University of New Mexico, Albuquerque, USA) and Prof. R.L. Wells (Prof. Emeritus, Duke University, Durham, USA) and results from some of these studies already have been published. Recent projects directed toward applications for GaN-based nanopowders have been carried out by our research group also in collaboration with Prof. B. Pałosz (Institute of High Pressure Physics, Polish Academy of Sciences, Warsaw, Poland) and Prof. M. Kamińska (Institute of Experimental Physics, Warsaw University, Warsaw, Poland).

### References

- [1] J.F. Janik, "Investigation of Group III–V compounds as precursors for solid state materials", PhD Dissertation, University of New Mexico, Albuquerque, NM, USA, 1987, p. 7.
  - [2] R.W. Rice, *Am. Ceram. Soc. Bull.* 62 (8) (1983) 889–892.
  - [3] For example, see reviews:
    - (a) J.L. Hudgins, *J. Electron. Mater.* 32 (6) (2003) 471–477;
    - (b) I. Akasaki, S. Kamiyama, H. Amano, *IEICE Trans. Electron. E85-C* (1) (2002) 2–9;
    - (c) T. Trindade, P. O'Brien, N.L. Pickett, *Chem. Mater.* 13 (2001) 3843–3858;
    - (d) S.J. Pearton, F. Ren, *Adv. Mater.* 12 (21) (2000) 1571–1580;
    - (e) S. Nakamura, *Mater. Sci. Eng. B43* (1997) 258–264;
    - (f) H. Morkoç, *Mater. Sci. Eng. B43* (1997) 137–146.
  - [4] For example, see:
    - (a) J. Arakawa, *IEICE Trans. Electron. E85-C* (1) (2002) 37–44;
    - (b) M. Ohtsu, K. Kobayashi, T. Kawazoe, S. Sangu, T. Yatsui, *IEEE J. Sel. Top. Quantum Electron.* 8 (4) (2002) 839–862;
    - (c) M. Green, *Curr. Opin. Solid State Mater. Sci.* 6 (2002) 355–363;
    - (d) O.I. Mičić, S.P. Ahrenkiel, D. Bertram, A.J. Nozik, *Appl. Phys. Lett.* 75 (4) (1999) 478–480.
  - [5] For example, see:
    - (a) R. Haubner, M. Wilhelm, R. Weissenbacher, B. Lux, *Struct. Bond.* 102 (2002) 1–45 (review);
    - (b) O. Fugunaga, *J. Phys.: Condens. Matter* 14 (2002) 10979–10982;
    - (c) E.A. Pruss, G.L. Wood, W.J. Kroenke, R.T. Paine, *Chem. Mater.* 12 (2000) 19–21;
    - (d) J.F. Janik, W.C. Ackerman, R.T. Paine, D.W. Hua, A. Maskara, D.M. Smith, *Langmuir* 10 (1994) 514–518.
  - [6] For example, see:
    - (a) R.L. Wells, W.L. Gladfelter, *J. Cluster Sci.* 8 (1997) 217–238;
    - (b) R.T. Paine, L.G. Sneddon, *Inorganic and Organometallic Polymers, II ACS Symp. Ser.* 572 (1994) 358–374 (and references therein).
  - [7] (a) J.F. Janik, E.N. Duesler, R.T. Paine, *Inorg. Chem.* 26 (1987) 4341–4345;
  - (b) J.F. Janik, E.N. Duesler, R.T. Paine, *Inorg. Chem.* 27 (1988) 4335–4337;
  - (c) R.T. Paine, J.F. Janik, C. Narula, *Mater. Res. Soc. Symp. Proc.* 121 (1988) 461–464.
- [8] J.F. Janik, E.N. Duesler, W.F. McNamara, M. Westerhausen, R.T. Paine, *Organometallics* 8 (1989) 506–514.
- [9] J.F. Janik, R.A. Baldwin, R.L. Wells, W.T. Pennington, G.L. Schimek, A.L. Rheingold, L.M. Liable-Sands, *Organometallics* 15 (1996) 5385–5390.
- [10] L.I. Halouoi, S.S. Kher, M.S. Lube, S.R. Aubuchon, C.R.S. Hagan, R.L. Wells, L.A. Coury Jr., *ACS Symp. Ser.* 622 (1996) 178–194 (and references therein).
- [11] J.F. Janik, R.L. Wells, P.S. White, *Inorg. Chem.* 37 (1998) 3561–3566.
- [12] For example, see:
  - (a) A.J. Downs (Ed.), *Chemistry of Aluminium, Gallium, Indium, Thallium*, 1st ed., Blackie Academic & Professional, 1993;
  - (b) W.L. Gladfelter, *Chem. Mater.* 5 (10) (1993) 1372–1388 (and references therein).
- [13] J.F. Janik, R.L. Wells, V.G. Young Jr., A.L. Rheingold, I.A. Guzei, *J. Am. Chem. Soc.* 120 (1998) 532–537.
- [14] G.L. Wood, E.A. Pruss, R.T. Paine, *Chem. Mater.* 13 (2001) 12–14.
- [15] J.F. Janik, R.L. Wells, J.L. Coffey, J.V. St. John, W.T. Pennington, G.L. Schimek, *Chem. Mater.* 10 (1998) 1613–1622.
- [16] J.F. Janik, R.L. Wells, *Chem. Mater.* 8 (1996) 2708–2711.
- [17] (a) G. Chaplais, S. Kaskel, *J. Mater. Chem.* 14 (2004) 1017–1025;
- (b) T. Oku, M. Kuno, E. Narita, *J. Phys. Chem. Solids* 65 (2004) 549–552;
- (c) L. Czepirski, J.F. Janik, E. Komorowska-Czepirska, R.L. Wells, *Adsorp. Sci. Technol.* 20 (8) (2002) 723–728.
- [18] J.F. Janik, M. Drygaś, C. Czosnek, M. Kamińska, M. Palczewska, R.T. Paine, *J. Phys. Chem. Solids* 65 (2004) 639–645.
- [19] M. Drygaś, J. Gosk, M. Kamińska, J.F. Janik, *Symposium on Nano and Giga Challenges in Microelectronics—Cracow 2004*, 2004 (September 13–17) Cracow, Poland, p. O48.
- [20] M. Drygaś, C. Czosnek, R.T. Paine, J.F. Janik, *Mater. Res. Bull.* (2005) in press.
- [21] M. Drygaś, J.F. Janik, to be presented at 16th European Conference on Diamond, Diamond-like Materials, Carbon Nanotub and Nitrides–Diamond 2005, September 11–16, 2005, Toulouse, France.
- [22] M. Drygaś, R.T. Paine, J.F. Janik, in preparation.
- [23] For example, see:
  - (a) Y. Oshima, T. Eri, M. Shibata, H. Sunakawa, K. Kobayashi, T. Ichihashi, A. Usui, *Jpn. J. Appl. Phys.* 42 (part 2, No. 1A/B) (2003) L1–L3;
  - (b) Y. Oshima, T. Eri, M. Shibata, H. Sunakawa, A. Usui, *Phys. Status Solidi, A Appl. Res.* 194 (2) (2002) 554–558.
- [24] For example, see:
  - (a) C.J. Lu, A.V. Davydov, D. Josell, L.A. Bendersky, *J. Appl. Phys.*, 94 (1) (2003) 245–253;
  - (b) P. Patsalas, S. Logethetidis, *J. Appl. Phys.*, 93 (2) (2003) 989–998;

- (c) S. Gautier, Ph. Kominou, P. Patsalas, Th. Kehagias, S. Logethaidis, C.A. Dimitriadis, G. Nouet, *Semicond. Sci. Technol.* 18 (2003) 594–601;
- (d) J.Z. Ren, G.A. Rose, R.S. Williams, C.H. Booth, D.K. Shuh, *J. Appl. Phys.* 83 (12) (1998) 7613–7617;
- (e) A.G. Baca, F. Ren, J.C. Zolper, R.D. Briggs, S.J. Pearton, *Thin Solid Films* 308–309 (1997) 599–606;
- (f) H. Sato, T. Minami, E. Yamada, M. Ishii, S. Takata, *J. Appl. Phys.* 75 (3) (1994) 1405–1409.