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

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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.

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

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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 inorganometallic 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,

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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:

$$X_3\mathbf{A} + \mathbf{B}Y_3 \rightarrow [X_3\mathbf{A}{\cdot}\mathbf{B}Y_3](\text{possible Lewis adduct}) \rightarrow XY\uparrow + [X_2\mathbf{A} - \mathbf{B}Y_2] \rightarrow XY\uparrow + [X\mathbf{A} - \mathbf{B}Y] \rightarrow XY\uparrow + \mathbf{AB}$$

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.