A simple single-source precursor route to the nanostructures of AlN, GaN and InN†

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In an effort to find a simple and common single-source precursor route for the group 13 metal nitride semiconductor nanostructures, the complexes formed by the trichlorides of Al, Ga and In with urea have been investigated. The complexes, characterized by X-ray crystallography and other techniques, yield the nitrides on thermal decompnsiation. Single crystalline nanowires of AlN, GaN and InN have been deposited on Si substrates covered with Au islands by using the complexes as precursors. The urea complexes yield single crystalline nanocrystals under solvothermal conditions. The successful synthesis of the nanowires and nanocrystals of these three important nitrides by a simple single-precursor route is noteworthy and the method may indeed be useful in practice.

Nanostructures of Al, Ga and In nitrides have received much attention because of their unique electrical and optical properties which are of technological interest. The high growth temperature of AlN and the low decomposition temperature of InN pose certain difficulties in processing these materials. However, nanostructures of these group 13 metal nitrides have been prepared by several methods, the most common one being the reaction of the metals (M = Al, Ga, In), their oxides or halides with NH3, N2, azides or nitrides. Other strategies include the thermal decomposition of [M(NMe2)3]3Cl or azido precursors and the reaction of Me3NCHSiMe3 with MCl3 or metal cupferronates. We were interested in developing a simple, common route to the nanostructures of AlN, GaN and InN based on a single-source precursor. Knowing that these nitrides can be prepared by the reaction of the metals or their compounds with urea in an NH3 or N2 atmosphere and that urea forms complexes with several metals, we have investigated the well-defined complexes formed by the urea with the trichlorides of Al, Ga and In as precursors, after characterizing the complexes by X-ray crystallography and other techniques. Significantly, the decomposition of the urea complexes under appropriate conditions does indeed yield nanowires, nanocrystals and other nanostructures possessing the desired properties.

The trichlorides of Al and Ga form isostructural complexes of the composition [M(H2NCONH2)3]Cl3 with the P-3c1 space group possessing a structure commonly found in many other metal-urea complexes (see Fig. 1a), with six urea molecules coordinating the metal. InCl3 on the other hand, forms a complex of the formula In(H2NCONH2)3Cl3 with the Pa-3 space group (Fig. 1b) with three urea molecules and three chlorines around the metal. The conformation is facial, as in the corresponding Mo derivative. The difference in the nature of the complexes formed by Al, Ga and In can be understood on the basis of the HSAB principle of Pearson. In all the complexes, N–H···Cl hydrogen bonds stabilize the structures. Infrared spectra showed the expected bands assignable to the vibrational modes of the complexes. Thermogravimetric analysis under N2 flow showed that the Al and Ga complexes yield AlN and GaN around 1000 and 800 °C respectively. The In complex, however, yields a mixture of InN and In2O3 at ca. 550 °C due to the inadequate proportion of urea, and exhibits a continuous weight loss above this temperature due to instability of InN. Taking an additional quantity of urea with the In-urea complex in the starting mixture, or carrying out the decomposition of the complex in a NH3 atmosphere yields pure InN.

Decomposition of [M(H2NCONH2)3]Cl3 (M = Al, Ga) over gold islands deposited on a Si(100) substrate (see Fig. 2a) under a flow of nitrogen (ca. 200 sccm) gives AlN and GaN nanowires at 1000 and 800 °C, respectively. Decomposition of

Fig. 1 Structures of (a) [Ga(H2NCONH2)3]Cl3 and (b) In(H2NCONH2)3Cl3.

† Electronic supplementary information (ESI) available: colour version of Fig. 1. See http://www.rsc.org/suppdata/jm/b5/b502887f/
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In(H₂NCONH₂)₃Cl₃ in NH₃ (ca. 100 sccm) gave InN nanowires at 550 °C. The yields of the nanowires deposited on the gold islands were close to 100%. We show scanning electron microscope (SEM) images of the AlN, GaN and InN nanowires in Fig. 2b–d respectively. All the nanowires have the hexagonal structure (Fig. 2e) and the nanowire diameter varies in the 20–100 nm range, with the lengths going up to a few microns. The lattice fringes in the high resolution transmission electron microscope (HREM) images in Fig. 2f–h reveal spacings of 2.66, 2.44 and 2.68 Å corresponding to the (100), (101) and (101) planes of the wurtzite structures of AlN, GaN, and InN respectively. The photoluminescence (PL) spectrum of the GaN nanowires at room temperature show band-edge luminescence centered around 370 nm (3.35 eV), consistent with the literature value. The AlN nanowires show a PL band around 420 nm due to the defect related states. The InN nanowires show an absorption band centered at ca. 0.7 eV which is now considered to be the intrinsic band gap of InN.⁵

Refluxing \([\text{Ga(H₂NCONH₂)₆}]\text{Cl₃}\) in n-trioctylamine (TOA, bp 365 °C) for ca. 24 h yields GaN nanocrystals. Figs. 3a, b show two different sets of particles with different sizes. It is gratifying that we obtain nanocrystals of 2–3 nm diameter, with a narrow size distribution (see inset in Fig. 3a). The crystallinity of the nanocrystals is confirmed by X-ray and electron diffraction. The powder XRD and the DIFFAX¹³ simulated patterns for the ca. 3 nm size nanocrystals were consistent with the wurtzite structure. The HREM image in Fig. 3c establishes the single crystalline nature, the lattice fringes showing a spacing of 2.8 Å due to the (100) planes of wurtzite GaN. The PL spectrum (Fig. 3d) of the ca. 3 nm particles shows two emission bands centered at around 380 and 340 nm whereas the spectrum (not shown here) of the ca. 15 nm particles shows only the band around 380 nm. The lower wavelength band is due to quantum confinement as shown recently.⁵ Refluxing \([\text{Al(H₂NCONH₂)₆}]\text{Cl₃}\) in TOA gave nanocrystals with hexagonal structure. Refluxing In(H₂NCONH₂)₃Cl₃ gave hexagonal InN nanocrystals in mixture with a small proportion of the oxide.

Solvolothermal decomposition of the urea-complex precursors in toluene in an autoclave yields all the nitride nanocrystals in the 375–450 °C range. While the urea-complex of Ga yielded hexagonal GaN nanocrystals, the complex of Al gave cubic AlN nanocrystals.⁴ We could obtain cubic GaN nanocrystals by decomposing the complex in the presence of excess urea. Cubic InN nanocrystals were also obtained on decomposition of the complexes with excess urea. It is noteworthy that we are able to obtain both hexagonal and cubic phases of these nitrides depending on the conditions of the decomposition of the complexes. Heating GaCl₃ in a large excess of urea gave rise to GaN onions, nanotubes and other structures. This aspect is under investigation.

In conclusion, we have demonstrated that urea complexes of the trichlorides of Al, Ga and In can be used effectively as single-source precursors to produce nanowires, nanocrystals and other nanostructures of AlN, GaN and InN.
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12 Lattice parameters for hexagonal AlN, a = 3.005 Å, c = 5.040 Å (JCPDS no. 08-0262); GaN a = 3.208 Å, c = 5.236 Å (JCPDS no. 02-1078). InN a = 3.527 Å, c = 5.733 Å (JCPDS no. 02-1450).