

Synthesis of Heterometallic Group 13 Nanoclusters and Inks for Oxide Thin-Film Transistors**

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We have recently reported high-yielding syntheses of two inorganic Group 13 metal-hydroxide nanoclusters: $[\text{Ga}_{13}(\mu_3\text{-OH})_6(\mu\text{-OH})_{18}(\text{H}_2\text{O})_{24}(\text{NO}_3)_{15}]$ ("flat" Ga_{13} , **1**, Figure 1) and $[\text{Al}_{13}(\mu_3\text{-OH})_6(\mu\text{-OH})_{18}(\text{H}_2\text{O})_{24}(\text{NO}_3)_{15}]$ ("flat" Al_{13}).^[1,2] The $\{\text{M}(\mu_3\text{-OH})_6\text{M}_6(\mu\text{-OH})_6\}$ central fragment of these clusters forms a planar core with six additional $\text{M}(\text{H}_2\text{O})_4$ groups bound to the core by two $\mu\text{-OH}$ bridges. The outer metal ions alternate above and below the plane formed by the central seven metal ions. Prior synthetic preparation of Group 13

metal-hydroxide compounds such as these has proven difficult. Their syntheses often require caustic or acidic conditions and elevated temperatures and pressures to provide clusters, often in low yields. Crystallization periods of months or even years are typical.^[3–6] Owing to these difficulties, relatively few discrete Group 13 metal-hydroxide clusters have been synthesized, though several striking examples of aluminum^[3,4,6,7] and gallium^[1,5,8,9] complexes have been reported. Both hydrated clusters and those stabilized by organic ligands are known, with a larger variety of ligand-supported clusters having been isolated, owing to enhanced stability resulting from lower charge density.^[3] In the case of these inorganic and ligand-supported compounds, neither heterometallic nor indium-containing clusters are known. However, in the case of Keggin- Al_{13} clusters, the central tetrahedral metal can be substituted, forming M_1Al_{12} structures ($\text{M} = \text{Al}$, Ga , or Ge , with others suggested).^[10–13] To our knowledge, no heterometallic Group 13 metal-hydroxide clusters with multiple substitution have been reported. Furthermore, the low-yielding, challenging syntheses often associated with these clusters have prevented attempts at exploring applications requiring large quantities of such compounds. In order to address synthetic difficulties and to explore the use of these clusters as precursors for materials, we have developed an improved synthesis of heterometallic Group 13 nanoclusters.

There has been recent interest in the use of nanoscale cluster precursors to synthesize new materials.^[14–17] The difficult syntheses of Group 13 metal-hydroxide clusters have mostly prevented their use in these applications. Most solution precursors for printed oxide films involve controlled hydrolysis of metal–organic compounds and the condensation of metal-hydroxo sols that are then pyrolyzed to form the oxide. Such films are beset by a variety of density, defect, and segregation issues relating to the inhomogeneous nature of the sol, retention of significant organic components, or oxygen nonstoichiometry associated with organic burnout. From this perspective, soluble all-inorganic, heterometallic hydroxo clusters, such as the "flat" M_{13} system, provide model precursors and an entirely inorganic, rapid, low-volume-loss condensation pathway, eliminating the aforementioned detrimental effects of organic moieties.

Herein, we present a new heterometallic gallium–indium cluster, $[\text{Ga}_7\text{In}_6(\mu_3\text{-OH})_6(\mu\text{-OH})_{18}(\text{H}_2\text{O})_{24}(\text{NO}_3)_{15}]$ ("flat" Ga_7In_6 , **2**, Figure 1). This compound can be synthesized reliably, in yields ranging from 25 % to 95 %, by utilizing two different nitroso additives.^[1,2] Clusters **1** and **2** can both be prepared in gram-scale quantities, which enables the unprecedented use of these nanoclusters as single-source solution precursors for the deposition of oxide-semiconductor thin

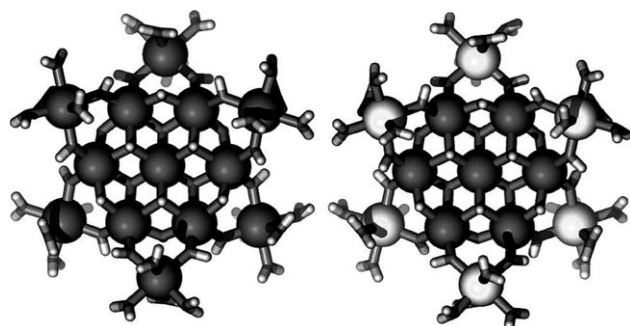


Figure 1. Representations of the molecular structures of $[\text{Ga}_{13}(\mu_3\text{-OH})_6(\mu\text{-OH})_{18}(\text{H}_2\text{O})_{24}(\text{NO}_3)_{15}]$ (**1**, left) and $[\text{Ga}_7\text{In}_6(\mu_3\text{-OH})_6(\mu\text{-OH})_{18}(\text{H}_2\text{O})_{24}(\text{NO}_3)_{15}]$ (**2**, right), determined by single-crystal X-ray diffraction. Ga and In are shown as dark and light spheres, respectively; hydroxo and aquo ligands are shown as stick representations.

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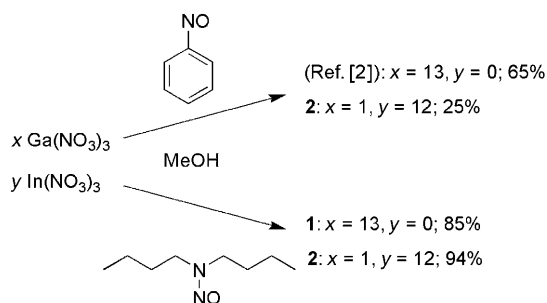
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films.^[18,19] Such deposition also provides a new route to the fabrication of high-performance thin-film transistors (TFTs), comprising spin-coated $\text{In}_{0.92}\text{Ga}_{1.08}\text{O}_3$ semiconductor layers.

Scheme 1 depicts synthetic routes to structures **1** and **2** using two different nitroso compound additives. Applying our previously reported procedure,^[1] using nitrosobenzene, to a



Scheme 1. Reaction conditions and the resulting yields for the synthesis of the Ga_{13} cluster **1**^[1] and the heterometallic Ga_7In_6 cluster **2**.

1:12 ratio of $\text{Ga}(\text{NO}_3)_3$ and $\text{In}(\text{NO}_3)_3$, afforded single crystals of cluster **2**, isolated in 25% yield. However, the manual separation of crystals from the tarlike product mixture limited the amount of material that could be isolated. To address the problems of difficult isolation and limited reaction scale, we sought alternatives to nitrosobenzene. The use of *N*-nitrosodi-*n*-butylamine affords **1** and **2** in superior yields of 85% and 95%, respectively.^[2] The reaction with *N*-nitrosodi-*n*-butylamine produces a transparent oil (which can be reused in future syntheses) from which gram-scale quantities of **1** and **2** can be easily isolated as single crystals. Multiple characterization techniques confirmed that the bulk crystals isolated from the reaction and the single crystals reported herein are the same.^[20] This robust synthetic strategy enables the use of these clusters as precursors for bulk materials.^[21]

For example, we have already begun exploring the use of these clusters in the fabrication of electronic devices, which is driven by a rising interest in printed macroelectronics and the high carrier mobilities recently reported in Group 13 and other *p*-block amorphous oxide semiconductors.^[18,22,23] We have recently described all-inorganic metal-hydroxo cation condensation routes to dense, high-quality oxide dielectric films.^[24,25] On the basis of these results, the discrete metal-hydroxide clusters **1** and **2** were immediately recognized as potential oxide precursors operating on similar principles. Cluster **2** is of particular interest because of the large indium fraction and the excellent performance of In_2O_3 -based semiconductors.^[22,23]

Initial device characteristics of a TFT with an amorphous $\text{In}_{0.92}\text{Ga}_{1.08}\text{O}_3$ (IGO) semiconductor derived from a spin-coated aqueous solution of **2** are presented in Figure 2; $V_{\text{on}} = -6$ V and limited hysteresis is observed. On-to-off current ratios are $>10^6:1$ for all devices fabricated on 100 nm thermally grown SiO_2 dielectric surfaces. Field-effect mobilities for these bottom-gate devices are approximately $9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ after annealing at 600°C . Characterization of similar, thicker films by X-ray diffraction results in the pattern

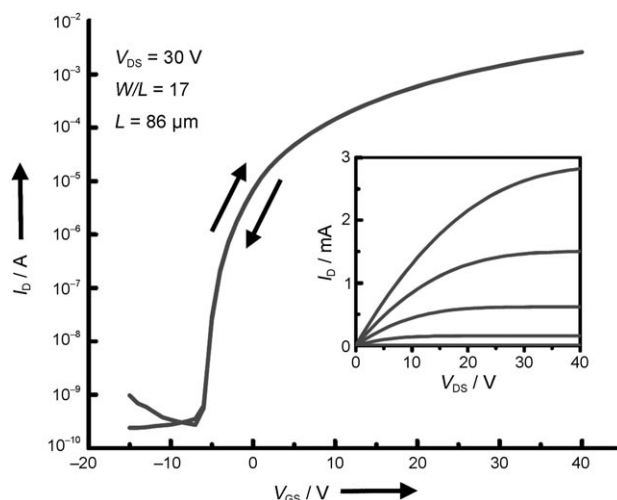


Figure 2. Representative transfer and (inset) output characteristics for a bottom-gate IGO-channel TFT with a 100 nm thermally grown SiO_2 dielectric surface. V_{GS} in the output curve is stepped from 0–40 V in 10 V steps. I_{D} = drain current; V_{DS} = drain-to-source voltage; V_{GS} = gate-source voltage; L = channel length; W = channel width

depicted in Figure 3. A single broad reflection centered near $2\theta = 33^\circ$ is consistent with previously reported amorphous IGO films.^[18] A cross-sectional image of the same film recorded by scanning electron microscopy (Figure 3, top)

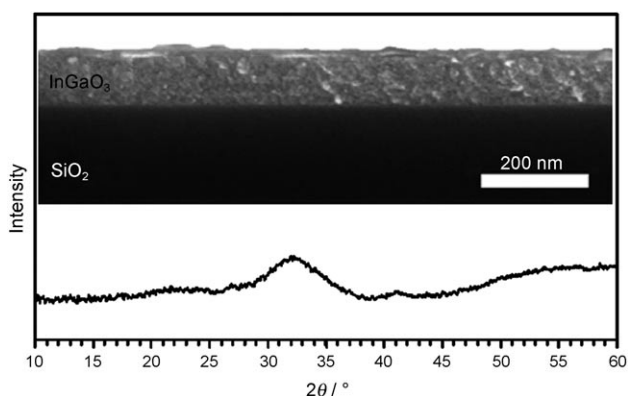


Figure 3. Thin-film XRD pattern and (top) cross-sectional SEM image of an $\text{In}_{0.92}\text{Ga}_{1.08}\text{O}_3$ film, spin-coated from an aqueous solution of **2** and annealed at 600°C for 1 h in air.

shows a generally dense morphology with small inhomogeneities (<10 nm) possibly resulting from agglomeration of subcolloidal species during spin-coating. The direct deposition of such high-performance semiconductors from aqueous solutions is unprecedented and represents an important step towards printed macroelectronics. Additional details on these devices and films will be reported in due course.

In summary, we have devised a synthetic strategy for making gallium clusters^[1] which utilizes a reusable reagent and proceeds relatively quickly, providing high yields of the cluster at ambient temperature. We have expanded this strategy and shown general utility by synthesizing aluminum clusters^[2] and heterometallic gallium/indium congeners. Inso-

far as these molecules might hold promise as single-source precursors for novel materials (as demonstrated by the IGO thin films reported herein), developing an efficient synthetic method is highly important. This work also perhaps sheds light on the mechanism of cluster growth. For example, previous work suggests that dimeric or octameric fragments might form initially.^[5] This synthetic method led to no structures with varying compositions of the inner seven metal atoms, suggesting the M_7 core might be particularly stable. A recent report of an analogous ligand-stabilized Fe₇ cluster supports this hypothesis.^[26]

Experimental Section

General: All chemicals were used as received: metal salts from Strem, *N*-nitrosodi-*n*-butylamine from TCI, and nitrosobenzene from Aldrich. Further experimental and X-ray diffraction details are provided in the Supporting Information.

[Ga₇In₆(μ₃-OH)₆(μ-OH)₁₈(H₂O)₂₄(NO₃)₁₅] (**2**): *N*-nitrosodi-*n*-butylamine (0.93 g, 5.9 mmol 24 equiv) was added to a solution of Ga(NO₃)₃ (0.068 g, 0.267 mmol, 1 equiv) and In(NO₃)₃ (0.872 g, 2.97 mmol, 12 equiv) in methanol (10 mL), forming a homogenous solution. The solvent was allowed to evaporate at room temperature over 2 weeks, affording single crystals of **2** (0.12 g, 94% yield with respect to gallium). *N*-nitrosodi-*n*-butylamine was removed using a syringe, and the remaining crystals were washed with cold EtOAc (three times) and dried in air. Using different Ga/In starting ratios produced clusters with compositions ranging from Ga₇In₆–Ga₁₂In₁. Further details will be presented in due course.

Thin films: Thin-film X-ray diffraction was performed on a Rigaku RAPID diffractometer with Cu_{Kα} radiation. TFTs were fabricated by dissolving **2** in deionized water having a resistance near 18 MΩ. The resultant ink was deposited by spin-coating on *p*-type Si substrates capped with a 100 nm layer of thermally grown SiO₂. Semiconductor/dielectric film stacks were then annealed for 1 h at 600 °C in air. Thermal deposition of Al source and drain electrodes through a shadowmask completed the device fabrication. TFTs were characterized in the dark using a Hewlett–Packard 4156C semiconductor parameter analyzer.

X-ray diffraction experiments were carried out on a Bruker Smart Apex diffractometer at 153 K using Mo_{Kα} radiation ($\lambda = 0.71073$ Å). C₆H₉₆Ga₇In₆N₁₅O₉₉ (2·6CH₃OH), $M_r = 3139.94$, $0.21 \times 0.18 \times 0.12$ mm, hexagonal, $R\bar{3}$, $a = 20.6974(14)$, $b = 20.6974(14)$, $c = 18.256(3)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$, $V = 6773(1)$ Å³, $Z = 3$, $\rho_{\text{calcd}} = 2.310$ g cm⁻³, $\mu = 3.704$ mm⁻¹, $F(000) = 4620$, $2\theta_{\text{max}} = 54.00^\circ$, $T = 153(2)$ K, 16375 reflections measured, 3290 reflections independent [$R_{\text{int}} = 0.0187$], $R1 = 0.0246$, $wR2 = 0.0721$ for 3290 reflections (165 parameters) with $I > 2\sigma(I)$, and $R1 = 0.0256$, $wR2 = 0.0727$, and $\text{GOF} = 1.102$ for all 3290 data, max/min residual electron density $+1.034/-0.406$ e Å⁻³.

CCDC 695541 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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