

## Solvothermal Co-reduction Route to the Nanocrystalline III–V Semiconductor InAs

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There has been much interest in synthesis and physical characterization of nanoscale semiconductors over the last several years. While most studies in the field have focused on II–VI semiconductors (CdS, CdSe),<sup>1–4</sup> the technological importance of III–V semiconductors (GaAs, InAs) makes a study of these materials more desirable.<sup>5,6</sup> However, investigations on III–V semiconductors have been largely restricted because of numerous difficulties with their preparation.

Conventional routes to III–V semiconductors include solid state reactions,<sup>7–9</sup> metalorganic chemical vapor deposition (MOCVD),<sup>10,11</sup> and molecular beam epitaxy (MBE).<sup>12,13</sup> Chemical conversion of monomeric arsenogallane to GaAs<sup>14</sup> and organometallic synthesis of GaAs<sup>6</sup> successfully avoid toxic AsH<sub>3</sub>. Until very recently, a solution-liquid-solid (SLS) growth method has been developed for crystallizing III–V semiconductors at a much decreased temperature.<sup>15</sup> Kher and Wells recently reported a new method for synthesizing GaP and GaAs, with the reaction of (Na/K)<sub>3</sub>E (E = P, As) and gallium halide solutions.<sup>16</sup> Organometallic reactions are successfully avoided in this method. Xie and co-workers used a similar reaction but introduced a benzene-thermal route to synthesize nanocrystalline GaN.<sup>17</sup>

However, all these reported routes require either high processing temperature or high post treatment temperature, or involve complex organometallic reactions and toxic gas, or need some extreme conditions such as an absolute nonaqueous non-oxygen environment.<sup>18</sup> Over the last several years, there have been considerable efforts to explore new solution routes to III–V semiconductors, with the goals of lowering processing temperature, avoiding complex reactions and toxic precursors, and searching for milder preparation conditions.

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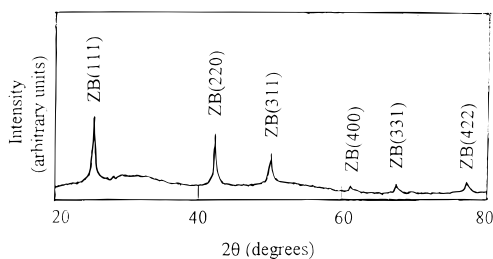


Figure 1. The XRD pattern of nanocrystalline InAs.

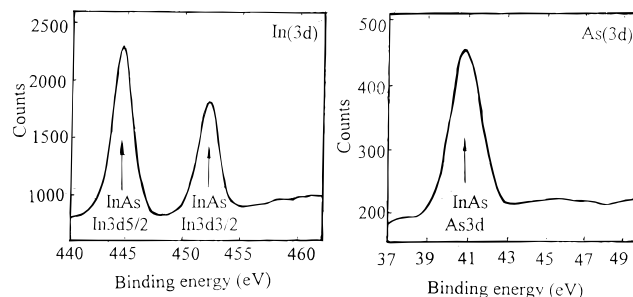
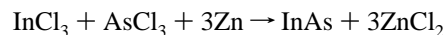


Figure 2. XPS spectra of the sample.

Herein we report a novel method for synthesizing the III–V semiconductor InAs. The reaction is carried out in a xylene solution at 150 °C and involves the simultaneous reduction of InCl<sub>3</sub> and AsCl<sub>3</sub>. The reaction can be formulated as follows:



We call it the solvothermal co-reductions (STCR) route. Nanocrystalline InAs with an average particle size of 15 nm is obtained by this route. The temperature used is to our knowledge the lowest at which crystalline InAs has been obtained, and complex organometallic reactions or the toxic gas AsH<sub>3</sub> used in conventional routes to III–V semiconductors has been completely avoided.

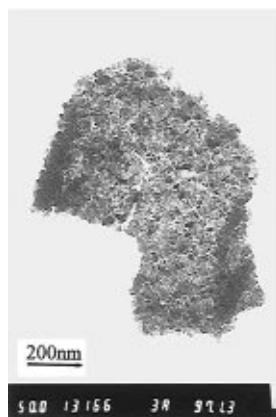
Analytically pure AsCl<sub>3</sub> and InCl<sub>3</sub> were mixed with xylene in appropriate proportions and put into an autoclave with zinc powder. The autoclave was kept at 150 °C for 48 h and then cooled to room temperature. A dark gray product was collected and washed with xylene, and then washed with dilute HCl aqueous solution. Finally, product was washed with absolute alcohol and desiccated in vacuum at 60 °C for 4 h.

X-ray powder diffraction (XRD) was carried out on a Rigaku D/max-rB X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). Figure 1 shows the XRD pattern of the sample. All the reflections in the figure can be indexed to be a pure zinc-blend (ZB) phase InAs with a lattice parameter a = 6.058, which is equal to literature value.<sup>19</sup> There is a small noncrystalline peak in the figure that can be attributed to the amorphous precursor. The average particle size of the product was determined by the Scherrer formula to be about 12 nm.

Elemental analysis by atomic absorption (PERKIN-ELMER 1100B Atomic Absorption Spectrophotometer) shows the presence of As and In in a 1.02:1.00 ratio. No zinc is detected in the sample.

Further evidence for the formation of InAs can be obtained from the X-ray photoelectron spectra (XPS) of the product. The XPS was recorded on a VGESCALAB MKII X-ray Photoelectron Spectrometer, using non-monochromatized Mg Kα X-ray as the excitation source, and the In(3d) and As(3d) core level regions were examined. Figure 2 shows the XPS spectra of the sample. The two strong peaks at 40.8 and 444.6 eV correspond to As(3d) and In(3d) binding energy, respectively,

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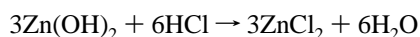
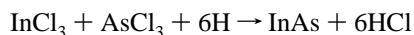
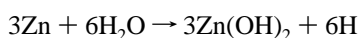


**Figure 3.** TEM image of the sample.

for InAs. No obvious peak for indium oxide (444.9 eV for In3d5/2 in In<sub>2</sub>O<sub>3</sub> and 445.0 eV in In(OH)<sub>3</sub>) or arsenic oxide (44.9 eV for As3d in As<sub>2</sub>O<sub>3</sub> and 46.2 eV in As<sub>2</sub>O<sub>5</sub>) is observed. The quantification of peaks gives the ratio of As to In of 51:49, which is consistent with that found by elemental analysis.

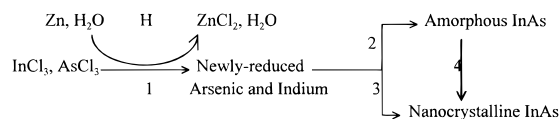
Figure 3 shows a transmission electron micrograph (TEM) image of the sample. The image was obtained with a Hitachi H-800 transmission electron microscope. We can observe some amorphous substance in the image, which can be attributed to the amorphous precursor. The image reveals that the average size of particles in the sample is about 15 nm. This is a bit larger than that obtained from the XRD patterns. The difference may be caused by the coexistence of the amorphous precursor. The size of the particles is hard to determine exactly.

In our route, no extreme conditions such as an absolutely nonaqueous, non-oxygen environment is required. Within the reducing environment caused by metallic zinc powder, the oxygen in the reaction system can be reduced to a negligible amount. A trace of water in the system proves not to be a serious problem. On the contrary, a small amount of water in the system may be helpful to the electron-transfer process of the reaction:



Atomic hydrogen generated by the reaction between zinc powder and water can act as a charge carrier during the co-reduction procedure. These experiments demonstrate that <1% (volume ratio) water in the reaction solution has no deleterious effect on the product. However, when the amount of water is increased to ca. 3%, an indium hydroxide (In(OH)<sub>3</sub>) phase obviously exists in the sample. It may be caused by hydrolysis of InCl<sub>3</sub>.

Figure 4 shows the schematic growth path of nanocrystalline InAs. With the co-reduction of AsCl<sub>3</sub> and InCl<sub>3</sub>, the newly-



**Figure 4.** Schematic growth path of nanocrystalline InAs.

reduced arsenic and indium are evenly dispersed in the solution. The reaction between them can result in two possible products, amorphous InAs and nanocrystalline InAs. In a conventional solution reaction, reaction 2 would be the main reaction and amorphous InAs is the dominant product. In a solvothermal system, the higher solvent temperature will favor reaction 3 and reaction 4. Nanocrystalline InAs becomes the major product. By increasing the processing temperature and solvent pressure further, reaction 3 and reaction 4 are favored more greatly. Consequently, a better crystallized product can be obtained. When the processing temperature is increased to 300 °C, a perfectly crystallized product is obtained.<sup>20</sup> To summarize, the co-reduction procedure provides newly-reduced and evenly-dispersed arsenic and indium, and the solvothermal system induces the reaction between them and promotes the crystallization process. A detailed study of the mechanism of the solvothermal co-reduction route is underway and will be reported elsewhere.

In conclusion, a novel solvothermal co-reduction (STCR) route to nanocrystalline InAs at a greatly decreased temperature has been developed. The temperature used is to our knowledge the lowest used to obtain nanocrystalline InAs up to now. The reaction conditions in our route are very easy to maintain. This is the first time that all goals (lower processing temperature, no organometallic reaction, no toxic gas, and no extreme conditions) have been realized, despite considerable efforts on the synthesis of III–V semiconductors in recent years.

The solvothermal co-reduction route may also be applicable to other III–V semiconductors such as GaAs and InSb, and even to some II–VI and IV–IV compounds. Further studies along these lines are in progress. It opens a new low-temperature way to synthesize highly covalent nonmolecular solid materials. Moreover, because of the simplicity of this route, it may potentially be applied on the scale of industrial production.

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**Supporting Information Available:** Figures of XRD pattern and TEM image and electron diffraction pattern of the sample prepared at 300 °C (1 page). See any current masthead page for ordering and Internet access instructions.

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(20) More detailed information concerning this can be obtained in the Supporting Information.