Chem. Mater. **1999,** *11,* 2619−2622

A Safe Low Temperature Route to InAs Nanofibers

Yi Xie,*[†,‡] Ping Yan,[‡] Jun Lu,[§] Wenzhong Wang,[‡] and Yitai Qian[†,‡]

Structure Research Laboratory, Department of Chemistry, and Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

Received May 26, 1999. Revised Manuscript Received June 30, 1999

InAs nanofibers were prepared at 160 °C through a new route: $2InCl_3 + 6KBH_4 + 2As \xrightarrow{\text{en}} 2InAs + 6KCl + 6BH_3 + 3H_2$. The products were characterized as zinc blende phase by X-ray powder diffraction (XRD). Transmission electron microscopy (TEM) images showed that the products were polycrystalline fibers or near-single-crystal whiskers with widths of 15−100 nm and lengths of 150−1000 nm. There is trace indium coexisting with the products, indicating that the reaction proceeds through a metallic indium intermediate. When the reaction temperature was lowered to 120 °C, which is below the melting point of indium, spherical InAs nanocrystals with diameters of 20−50 nm were prepared. A solution−liquid−solid (SLS) mechanism is proposed for the fiber growth. The composition of the products was analyzed by X-ray photoelectron spectroscopy (XPS).

Introduction

The III−V (13−15) compound semiconductors are well-known electronic and optoelectronic materials.[1] Recently, considerable effort has been expended on preparation and characterization of semiconductor nanocrystals for their novel electronic structures and optical properties.[2] While most studies in the field have focused on II−VI semiconductors (CdS, CdSe),[3] the technological importance of III−V semiconductors (GaAs, InAs) makes a study of these materials more desirable.[4,5] The present zeal for new routes to III−V compound semiconductors is motivated by several goals such as safe precursors and a low reaction temperature.[6] Several new strategies emerged in the last decade.[7] These strategies include dehalosilylation and related reactions,[8] a metathesis reaction,[9] pyrolysis of single-source precursors that incorporate the elements of a compound in a single molecule,[10] and so on. Although these methods are very mild in comparison with conventional solid state reactions (usually above 1000 °C), they still require a relatively high processing temperature or posttreatment temperature (200−500 °C) to obtain fully crystallized products.

Very recently, a solution−liquid−solid (SLS) mechanism was developed to grow well crystallized III−V semiconductor fibers at much decreased temperatures (111−203 °C for InP; 203 °C for InAs and GaAs).[11] The SLS is closely analogous to the well-known vapor−liquid−solid (VLS) mechanism,[12] in which whisker crystals grow from flux droplets that are fed from the vapor phase rather than a solution phase. The reaction employed in the SLS growth is described in eq 1.

$$(t\text{-Bu})_3In + AsH_3 \xrightarrow{\substack{\text{flux, 203 °C,}\\ \text{hydrocarbon,}\\ \text{10 mol \% XH}}} InAs + 3(t\text{-Bu})H \qquad (1)$$

The use of AsH_3 is of particular concern due to its carcinogenic and mutagenic properties. Considering the order of toxicity given by Penrose,[13] R_3As (R═H, Me, Cl, etc.) > As_2O_3 (As(III)) > $(RAsO)_n$ > As_2O_5 (AS(V)) > $R_nAsO(OH)_{3-n}$ (n = 1, 2) > R_4As^+ > As(0), we give a safer route in eq 2. A further advantage of this route is that the reactants are readily available.

$$2InCl_3 + 2As + 6KBH_3 \xrightarrow{\text{ethylenediamine}} 2InAs + 6KCl + 6BH_3 + 3H_2 \quad (2)$$

[†] Structure Research Laboratory, University of Science and Technology of China.

[‡] Department of Chemistry, University of Science and Technology of China.

[§] Department of Chemical Physics, University of Science and Technology of China.

(1) Streetman, B. G. *Solid State Electronic Devices,* 3rd ed.; Prentice Hall: Englewood Cliffs, NJ, 1990.

(2) Alivisatos, A. P. *Science* **1996**, *271*, 933.

(3) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706. (b) Katari, J. E. B.; Colvin, V. L.; Alivisatos, A. P. *J. Phys. Chem*. **1994**, *98*, 4109.

(4) Olshavsky, M. A.; Goldstein, A. N.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1990**, *112*, 9438.

(5) Li, Y.; Duan, X.; Qian, Y.; Yang, L.; Ji, M.; Li, C. *J. Am. Chem. Soc.* **1997**, *119*, 7869.

(6) Buhro, W. E. *Polyhedron* **1994**, 13, 1131.

(7) For a recent review, see: Wells, R. L.; Gladfelter, W. L. *J. Cluster Sci.* **1997**, *8*, 2.

(8) Wells, R. L.; Aubuchon, S. R.; Kher, S. S.; Lube, M. S.; White, P. S. *Chem. Mater.* **1995**, *7*, 793. (b) Uchida, H.; Matsunaga, T.; Yoneyama, H.; Sakata, T.; Mori, H.; Sasaki, T. *Chem. Mater.* **1993**, *5*, 716.

(9) Treece, R. E.; Macala, G. S.; Rao, L.; Franke, T.; Eckert, H.; Kaner, R. B. *Inorg. Chem*. **1993**, *32*, 2745. (b) Kher, S. S.; Wells, R. L. *Chem. Mater*. **1994**, *6*, 2056. (c) Xie, Y.; Qian, Y.; Wang, W.; Zhang, S.; Zhang, Y. *Science* **1996**, *272*, 1926.

(10) Cowley, A. H.; Jones, R. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1208. (b) Green, M.; O'Brien, P. *Chem. Commun.* **1998**, 2459.

(11) Trentler, T. J.; Hickman, K. M.; Goel, S. C.; Viano, A. M.; Gibbons, P. C.; Buhro, W. E. *Science* **1995**, *270*, 1791. (b) Trentler, T. J.; Goel, S. C.; Hickman, K. M.; Viano, A. M.; Chiang, M. Y.; Beatty, A. M.; Gibbons, P. C.; Buhro, W. E. *J. Am. Chem. Soc.* **1997**, *119*, 2172.

(12) Wagner, R. S. In *Whisker Technology*; Levitt, A. P., Ed.; Wiley: New York, 1970; Chapter 3.

10.1021/cm9903327 CCC: $18.00

Reduction of metal salts with hydroorganoborates has been used to prepare finely divided powders of metals and alloys (see eq 3).[14] We have extended it to prepare MSe (M = Cd et al.)[15] at room temperature and InP[16] nanocrystals at 80−160 °C. In this paper we exploit potassium borohydride reducing route to prepare InAs spherical nanocrystals and nanofibers.

$$uMX_v + vM'(Br_3H)_u \xrightarrow{THF} uM + vM'X_u + vBR_3 + (uv/2)H_2 \quad (3)$$

Experimental Section

A. Synthesis of InAs Nanocrystals. All reagents were of analytical grade or better and were used without further purification. A typical synthesis is as follows: 40 mL of ethylenediamine,0.375 g (5 mmol) of As, 1.107 g (5 mmol) of $InCl_3$ and 0.807 g of KBH_4 (15 mmol) were added to a 50 mL flask, and then the mixture was ultrasonically mixed for 4 h before being transferred to a Teflon-lined autoclave. The autoclave was kept at 100, 120, or 160 °C for 24 h, respectively, and then cooled to room-temperature naturally. The products were filtered out, washed with absolute alcohol, 1 N HCl, and distilled water in subsequence, and then dried in a vacuum at room temperature for 4 h.

B. Structural Characterization. Powder X-ray diffraction (XRD) patterns were obtained on a Rigaku D/MaxγA rotation anode X-ray diffractometer with Ni-filtered Cu Kα radiation (λ = 1.541 78 Å). Transmission electron microscopy (TEM) measurements were made on a Hitachi H-800 transmission electron microscope with an accelerating voltage of 200 kV. Samples were deposited from ethanol solution of the products onto thin amorphous carbon films supported by copper grids.

The product purity and composition were detected by X-ray photoelectron spectra (XPS) recorded on an ESCALabMKII instrument with Mg Kα radiation as the exciting source. The binding energies obtained in the XPS analysis were corrected by referencing the C 1s line to 284.60 eV.

Results and Discussion

Reaction of $InCl_3$, arsenic, and potassium borohydride at 100−160 °C in ethylenediamine resulted in black precipitates. X-ray powder diffraction (XRD) pattern of the samples agrees well with the bulk InAs reflections indicating the same zinc blende lattice structure (Figure 1).[17] Average crystallite sizes estimated by the Scherrer equation based on half-width of XRD peaks are about 25 nm.

The reaction temperature is a critical factor in this approach. At room temperature the reaction did not initiate at all; at temperatures from 100 to 160 °C the yield of InAs increased with temperature, while the indium content decreased with temperature (Figure 1a−c). Phase-pure products can be obtained after treatment with 1 N HCl (Figure 1d,e). These facts led us to believe the chemical pathway is as follows:

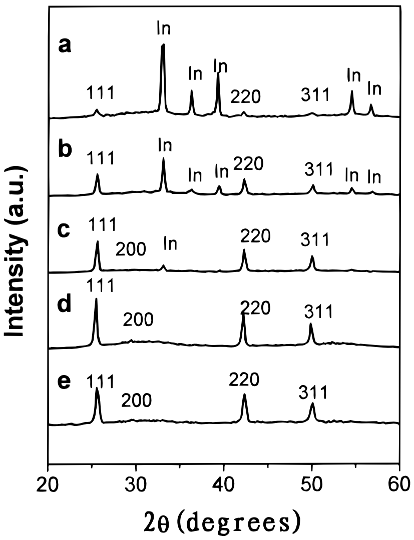

Figure 1. XRD patterns of the products: (a) 100 °C, before 1 N HCl treatment; (b) 120 °C, before 1 N HCl treatment; (c) 160 °C, before 1 N HCl treatment; (d) 120 °C, after 1 N HCl treatment; (e) 160 °C, after 1 N HCl treatment.

$$2InCl_3 + 6KBH_4 \rightarrow 2In + 6KCl + 6BH_3 + 3H_2 \quad (4)$$

$$2In + 2As \rightarrow 2InAs \quad (5)$$

All the above facts can be rationalized as follows: at room temperature, even the first step cannot take place; when the reaction temperature is as low as 100 °C, the freshly formed indium reacted with arsenic to a very small extent; when the reaction temperature is raised to 160 °C, which is above the melting point of indium (T_{mp} = 156.4 °C), the reaction is rather complete and only trace indium coexisted in the product.

Transmission electron microscopy (TEM) images for the samples are shown in Figure 2. When the reaction temperature is 160 °C, the products are polycrystalline fibers or near-single-crystal whiskers with a diameter of 15−100 nm and lengths of 150−1000 nm. Selected area diffraction within linear segment of a whisker (marked with an arrow) gave single-crystal patterns, which could be indexed for the [13$\bar{4}$] zone axis of crystalline InAs and suggested that the whisker axis was the [111] direction (Figure 2b). Whiskers of cubic compounds (such as III−V semiconductors)[11] and elements (such as Si)[18] obtained from VLS and SLS processes typically grow along the [111] direction. When the reaction take place at 120 °C, the products are spherical grains with diameters from 20 to 50 nm, the electron diffraction pattern (Figure 2d) gave diffraction rings indexed to zinc blende InAs.

The SLS mechanism, which was recently reported by Buhro and co-workers in the preparation of III−V nanowhiskers and nanofibers, is very likely to function under the present condition because both cases involved reactions inorganic solvent, and in both cases indium coexisted with the products. Since the SLS mechanism cannot function without liquid indium, reaction at a temperature below the melting point of indium (156.4 °C) should not give whiskers or fibers. The failure to obtain whiskers or fibers at 120 °C further confirmed the proposed mechanism. Similar results were obtained incase of InP.[16]

---

(13) Penrose, W. R. *CRC Crit. Rev. Environ. Control* **1974**, 465.

(14) Bönnemann, H.; Brijous, W.; Joussen, T. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 273.

(15) Wang, W.; Geng, Y.; Yan, P.; Liu, F.; Xie, Y.; Qian, Y. *J. Am. Chem. Soc.* **1999**, *121*, 4062.

(16) Yan, P.; Xie, Y.; Wang, W.; Liu, F.; Qian, Y. *J. Mater. Chem.* **1999**, *9*, 1831.

(17) Joint Committee on Powder Diffraction Standards (JCPDS), File No. 15-869, InAs.

(18) Morales, A. M.; Lieber, C. M. *Science* **1998**, *279*, 208.

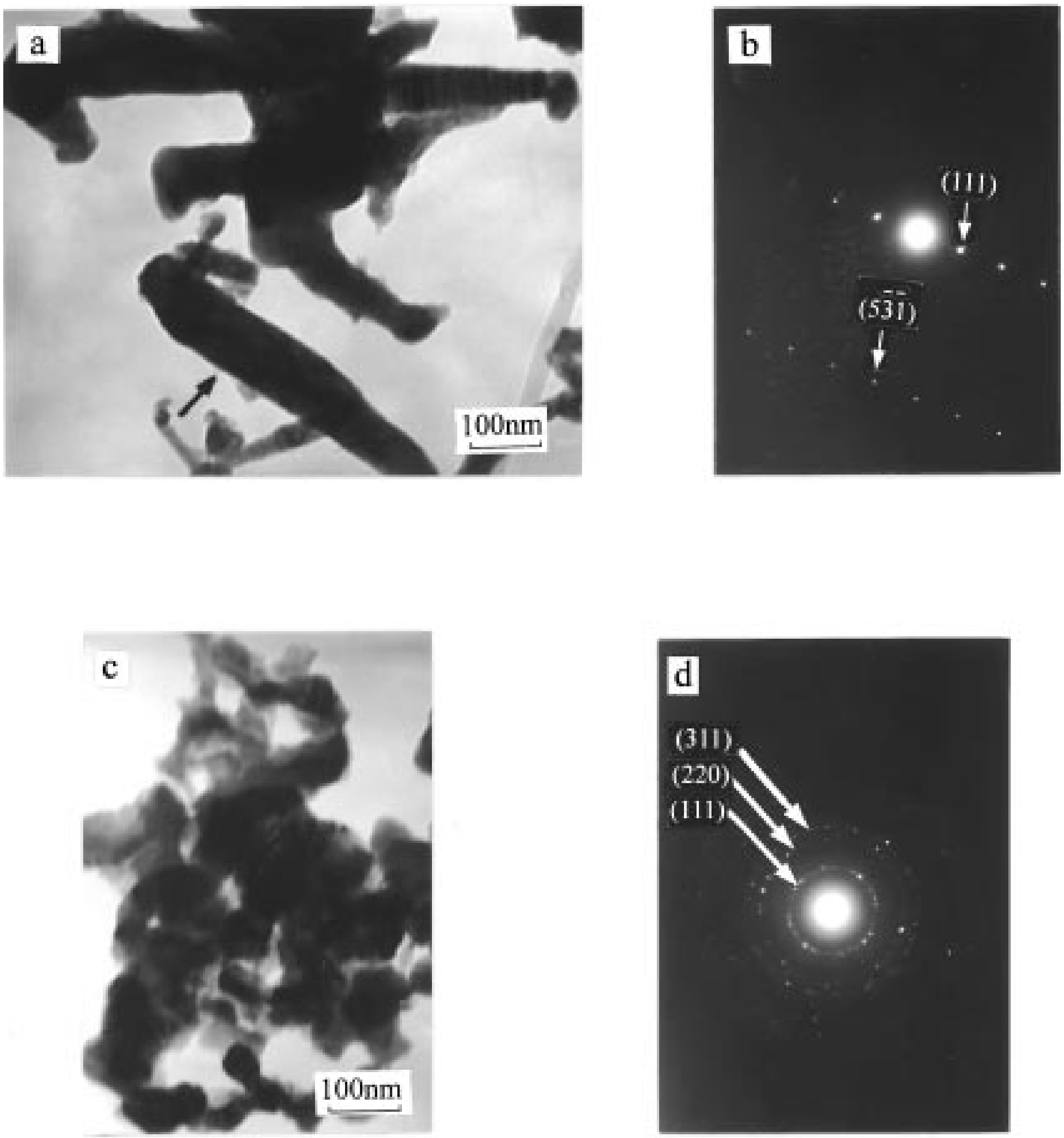

Figure 2. (a) TEM images for InAs nanofibers prepared at 160 °C. (b) Selected area electron diffraction pattern recorded along the $[13\bar{4}]$ zone axis perpendicular to the nanowhisker growth axis. (c) TEM images for InAs nanocrystals prepared at 120 °C. (d) Selected area electron diffraction pattern for the products prepared at 120 °C.

X-ray photoelectron spectroscopy (XPS) has been used to measure the elemental composition of the as-prepared nanocrystals and examine the oxidation of the nanocrystal surface. A survey spectrum is shown in Figure 3. The survey indicates the presence of In and As as well as C from reference and O from absorbed gaseous molecules. Otherwise the spectrum is quite clean because there are no peaks for Cl or N from the reactants.

Higher resolution spectra were also taken of the In 3d region and As 3d regions (Figure 4). The indium core is spin−orbit split to $3d_{5/2}$ and $3d_{3/2}$ with the $3d_{5/2}$ peak at 444.7 eV. The As 3d core also shows two peaks, one at 42.0 eV corresponding to As from InAs and the other at about 44.6 eV corresponding to oxidized As species. Similar results have been observed by other authors in InP nanocrystals.[19]

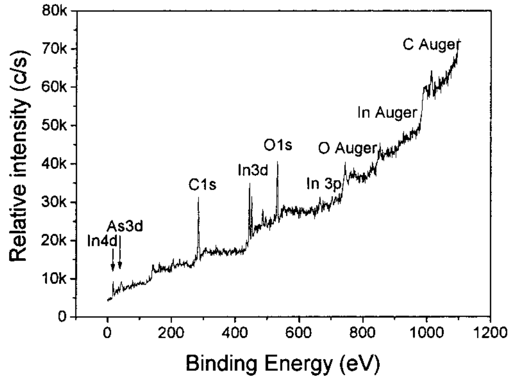

Figure 3. XPS survey spectra for InAs nanofibers.

Peak areas of these high-resolution scans were measured and used to calculate the In-to-As ratio for the nanocrystals. Quantification, in which only the As 3d peak corresponding to InAs was used, gives an In-to-As ratio of 1:1.1. As mentioned above, there was trace

---

[19] Guzelian, A. A.; Katari, J. E. B.; Kadavanich, A. V.; Banin, U.; Hamad, K.; Juban, E.; Alivisatos, A. P.; Wolters, R. H.; Arnold, C. C.; Heath, J. R. *J. Phys. Chem.* **1996**, *100*, 7212.

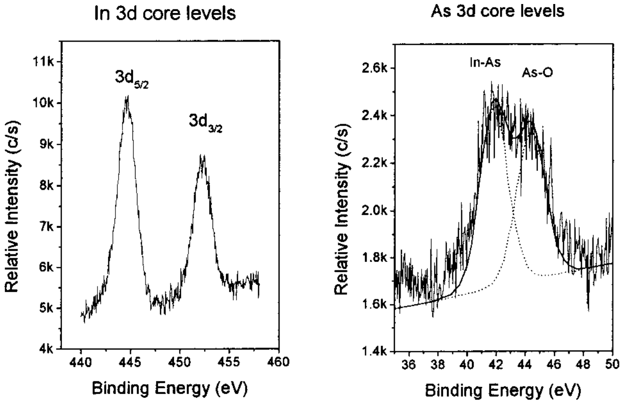

Figure 4. High-resolution XPS scans of the In 3d and As 3d cores for InAs nanofibers. The In 3d core is spin−orbit split into $3d_{5/2}$ and $3d_{3/2}$ peaks. The As core region has two peaks, one at 42.0 eV due to As bound to indium and the other at 44.6 eV due to oxidized species.

indium removed by 1 N HCl, so it is no wonder that more As atoms than In occupied the surface sites of the product. This excess arsenic is also responsible for the oxidized As 3d peak at 44.6 eV. Thus, we conclude that the nanocrystals are close to stoichiometric.

Conclusion

InAs fibers with widths of 15−100 nm and lengths of 150−1000 nm were successfully synthesized via a novel reaction of $InCl_3$, As, and KBH_4 in ethylenediamine at temperature of 160 °C for 24 h. The reaction proceeds with indium as the intermediate. The SLS mechanism is likely responsible for the fiber growth.

Acknowledgment. Financial support from the Chinese National Foundation of Natural Science Research through the Outstanding Youth Science Fund and Huo Yingdong Foundation for Young Teachers is gratefully acknowledged.

CM9903327