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InP nanowires from surfactant-free thermolysis of single molecule precursors[†]‡

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Indium phosphide nanofibres were grown from a single-molecule precursor, $[(PhCH_2)_2InP(SiMe_3)_2]_2$, using hot injection techniques by a solution–liquid–solid (SLS) process, under "surfactant-free" conditions and without the use of protic additives. The fibres are 85–95 nm in diameter and grow from In metal droplets of 100 nm diameter. The length of the nanofibres is a function of the precursor injection temperature (rather than the growth temperature) and can be varied from 6000 nm at 210 °C to 1000 nm at 310 °C. The indium metal tip can be readily removed under mild, non-etching conditions by treatment with thiophenol–P(SiMe₃)₃ mixtures.

Introduction

Group III-V semiconductor nanowires (NWs) are of interest in applications such as optical devices, solar cells, interconnects, plastic electronics and others.^{1–7} Several methodologies for their synthesis have been developed, including vapour-liquid-solid (VLS),^{8,9} solution–liquid–solid (SLS),¹⁰ laser catalytic growth (LCG),^{11,12} oxide assisted growth^{13,14} and templating strategies.^{15,16} The low toxicity of compounds such as InP compared to CdSe nanostructures is a particular attraction. A number of wet chemical methods for the bottom-up synthesis of InP NWs have been reported. For example, Buhro et al. used mixtures of In^tBu₃ and PH₃ in the presence of protic reagents, as well as the methanolysis of ['Bu₂InP(SiMe₃)₂]₂, to obtain InP fibres of 10-100 nm diameter. They demonstrated that the protic additive, methanol, cleaves the In-P and P-SiMe₃ bonds, generating ['Bu₂In(OMe)]₂ and ['Bu₂In(PH₂)]₃ as intermediates. Nanofibre growth occurred from In metal nanodroplets formed by reduction of some of the precursor, and *tert*-alkyl substituents in particular were thought to be linked to this reductive decomposition pathway.^{10,17} Ahrenkiel et al. used a mixture of two molecular precursors, viz. $[{}^{t}Bu_{2}InP(SiMe_{3})_{2}]_{2}$ and $[Cl_{2}InP(SiMe_{3})_{2}]_{2}$ together with donor surfactants such as dodecylamine and trioctylamine in the presence of trioctylphosphine (TOP), trioctylphosphine oxide (TOPO) and MeOH at temperatures of up to 250 °C. These authors found the indium chloride precursor to be

necessary to reduce the size of the In metal droplets, while In'Bu₃ precursors at 330 °C gave tadpole-like InP fibres attached to large indium metal droplets.¹⁸ According to Fang *et al.* a similar temperature regime is required to generate In/InP nanowires from InMe₃ and P(SiMe₃)₃ in octadecene (ODE) in the presence of myristic acid. Clean production of nanowires was observed >280 °C, while at lower temperatures a mixture of nanoparticles and nanowires was produced and no wire growth was seen at 260 °C.¹⁹ By contrast, Weller and co-workers recently reported the growth of In/InP nanorods from InMe₃ and trioctylphosphine in the presence of TOPO at the much lower optimum growth temperature of 200 °C, while higher temperatures increased the size of the In droplets an led to multiple nanorod growth per droplet.²⁰

In this paper we describe a fast and simple route to clean-surfaced InP nanofibres using a hot injection technique, without the addition of strongly binding surfactant stabilisers and in the absence of protic reagents and carboxylic acids. The lengths of these wires could be easily controlled by adjusting the injection temperature.

Results and discussion

The indium dibenzyl single-molecule precursor $[(PhCH_2)_2InP-(SiMe_3)_2]_2$ (1) was chosen as a halide-free starting material, initially in the expectation that reductive elimination of the benzyl substituents might be more facile than the decomposition of 'Bu derivatives and might therefore result in a reduction of the initiation temperature. The compound is readily prepared from InCl₃, benzyl Grignard and P(SiMe_3)_3; the crystal structure is shown in Fig. 1.

Thermolysis of **1** on injection into hot methyl myristate leads to two decomposition processes, the reduction of In(III) to In(0) which gives nanosized metal droplets, and the formation of indium phosphide, which grows as fibres from the molten metal surface. Thermogravimetric analysis (Fig. 2) shows that **1** incurs

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Fig. 1 Molecular structure of $[(PhCH_2)_2InP(SiMe_3)_2]_2$ (1), showing the atomic numbering scheme. Selected bond lengths (Å) and angles (°): In–P 2.6085(5); In–P' 2.6160(4); In–C(3) 2.2279(15); In–C(4) 2.2013 (14); P–In–P' 86.652(14); In–P–In' 93.348(14); C(3)–In–C(4) 110.00(6).



Fig. 2 TGA diagram of $[(PhCH_2)_2InP(SiMe_3)_2]_2$; heating rate 10 °C min⁻¹ (N₂ flow rate 60 cm³ min⁻¹).

a 66% weight loss on heating to 209 °C, probably due to the loss of volatiles such as $PhCH_2SiMe_3$, $PhCH_2CH_2Ph$ and $PhCH_2P(SiMe_3)_2$ (which approximate to 72 wt%), and shows that formation of InP and In(0) occurs at this temperature. While it was not our objective to determine the decomposition mechanism, under the high temperature conditions two competing decomposition pathways seem likely, leading to In metal and InP, respectively:

$$\begin{split} \left[(\text{PhCH}_2)_2 \text{InP}(\text{SiMe}_3)_2 \right]_2 & \rightarrow 2\text{PhCH}_2 \text{P}(\text{SiMe}_3)_2 \\ & + \text{PhCH}_2 \text{CH}_2 \text{Ph} + 2\text{In}^0 \end{split}$$

$$[(PhCH_2)_2InP(SiMe_3)_2]_2 \rightarrow 4PhCH_2SiMe_3 + 2InP$$

Growth will then take place from InP dissolved on the surface of liquid In droplets.

The observation of facile nanofibre growth in non-protic media differs from the report by Fang *et al.* who found myristic acid to be necessary for nanowire growth, while in its absence mainly InP nanoparticles were obtained.¹⁹ We believe these differences may be due to the use of single-molecule precursors



Fig. 3 Dependence of InP NW average lengths with growth temperature.

in our case, which provide for a different reaction path to InP formation.

The formation of NWs depends on the minimum injection temperature of 210 °C, but not on the growth temperatures. No NWs resulted if the injection temperature was below 210 °C, but they can be grown even at 160 °C once sufficient nucleation has taken place.

Effect of temperature

The morphology of nanowires can depend on many factors, such as the concentration of the precursors, growth duration, temperature, and concentration of surfactants. Although empirical results have been published in the past showing a dependence of the diameter of nanowires on temperature,¹⁹ to the best of our knowledge the effect of the growth temperature on the lengths of nanowires has not been systematically investigated. The results are shown in Fig. 3.

The length of the InP nanofibres decreases with rising injection temperature. As the temperature increases, so does the number of indium nanodroplets, at the expense of InP growth, resulting in shorter fibres being formed at higher temperatures. Fig. 4 shows the TEM images of nanofibres grown at three different injection temperatures, *viz.* low (210 °C), medium (240 °C) and high (310 °C).

Morphology and microstructure

The nanowires synthesized by this method were several μ m long but with fairly constant diameters of 85–95 nm at all temperatures. In their as-made state they are attached to indium metal particles of *ca.* 100 nm diameter. Electron diffraction studies show that the lattice parameters of these fibres match those of cubic InP. Fig. 5 shows the X-ray diffraction (XRD) pattern of a typical sample of InP nanofibres and confirms the presence of both InP and In metal.

Fig. 6 shows a high-resolution TEM micrograph of a typical nanofibre. The <001> lattice fringes of the InP (zinc blende structure) are well aligned and the nanowire grew apparently along its unit cell axes. The distance between 10 lattice fringes is 2.9 nm, which corresponds well with the expected value of



Fig. 4 TEM micrographs of InP nanofibres synthesized at injection temperatures of 210, 240 and 310 °C.



Fig. 5 X-ray diffraction pattern of InP nanofibres. Red: InP reflections (card no. 70-2902); blue: In metal reflections (card no. 05-0642).

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2.844 nm (InP has a lattice constant of 0.5688 nm). There was no evidence for an oxide or amorphous surface layer.

The nanowires formed were very stable, even in absence of any surfactants. The solvent has no influence over the growth process, as the same morphology was obtained from reactions conducted in methyl myristate and in a non-coordinating solvent, 1-octadecene (ODE), although in the latter case the uniformity of the wires was slightly poorer.

Removal of the In metal tip

The indium metal attached to the nanowires can act as charge acceptor and affect the physical properties of the wires. Thus the presence or absence of the metal tips becomes potentially important. Buhro *et al.* used metallic bismuth for NW growth,²¹ whereas, Ahrenkiel *et al.* used indium metal particles as seeds to grow InP nanorods.¹⁸ In both cases etching techniques have been used for metal removal, which not only dissolved the metal



Fig. 6 HRTEM micrograph of a single InP nanofibre, showing the <001> lattice planes and distance corresponding to cubic InP.

but also corroded the surface of the nanorods. Moreover, Ahrenkiel's procedure also involves the use of HF and mercury.

We found that the metal tip can be conveniently removed in a one-pot reaction by utilizing the reactivity differences between InP and In metal towards P(SiMe₃)₃. When P(SiMe₃)₃ was added to the solution of pre-formed nanowires in the presence of reagent capable of protolysing the P-Si bonds, in this case thiophenol, at a temperature well above the melting point of indium metal (m.p. 156.6 °C), the metal droplets were converted to InP nanoparticles. The reducing nature of this process means that any oxide layer that may be present is also removed. Heating the mixture above the melting point of indium is necessary for efficient conversion into InP nanoparticles under these conditions. Fig. 7 shows the TEM micrograph of the metal-free InP nanowires. The inset image confirms that there is no indium left at the base of an individual wire. There was no evidence that removal of the In tip affected the length of the nanowires. Some twisting occurred after several washing and purification procedures. XRD confirmed that the wires are composed of InP, with no evidence for the presence of In_2S_3 .

Conclusions

The thermal decomposition of dialkylindium phosphide singlesource precursors in hot weakly or non-coordinating solvents provides a simple, surfactant-free method for the growth of InP nanowires. This reduces the scope of any lattice doping by heteroatoms. To the best of our knowledge, such surfactant-less growth of nanowires synthesized through the SLS mechanism has not previously been reported.^{21–25} The synthesis is fast, at the time scale of minutes, and gives high-quality crystalline wires. The method avoids the need for preparing metal seed particles to induce NW growth. The lengths of the nanofibres can be conveniently controlled by adjusting the injection



Fig. 7 TEM image showing InP nanofibres (grown at 250 $^{\circ}$ C) after removal of In metal particles.

temperature, from about 1000 nm at 320 $^{\circ}$ C to 6000 nm at 210 $^{\circ}$ C. No growth was observed at injection temperatures below 210 $^{\circ}$ C. The indium metal tip can be removed under mild conditions by conversion to InP nanoparticles, which are readily separated by centrifugation. We are currently exploring potential applications of these intriguing materials.

Experimental section

All manipulations were performed under dry nitrogen, using standard Schlenk techniques. Solvents were pre-dried over sodium wire and distilled under argon over sodium (toluene), sodium-potassium alloy (light petroleum, bp 40-60 °C), or sodium-benzophenone (diethyl ether, diphenyl ether). Dichloromethane was dried over calcium hydride. Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze-thaw cycles. InCl₃ (Aldrich 98%) was used as received, P(SiMe₃)₃ was prepared following a literature procedure.²⁶ Methyl myristate was dried over molecular sieves and degassed by several freeze-thaw cycles. ¹H and ³¹P NMR spectra were recorded using a Bruker DPX300 spectrometer. Transmission electron microscopy (TEM) images were recorded using a JEM-2000 EX Electron Microscope (Jeol Ltd) at 200 kV; TEM samples were prepared by placing InP nanowires dispersed in dichloromethane on 300 mesh copper grids with Holey carbon films. Thermogravimetric analysis was conducted using a Hi-Res TGA 2950 instrument (TA Instruments).

Synthesis of [(PhCH₂)₂InP(SiMe₃)₂]₂ (1)

To a suspension of $InCl_3$ (1.52 g, 6.86 mmol) in 50 mL dry diethyl ether at -78 °C was added freshly prepared PhCH₂MgCl in Et₂O (1.14 M, 12.04 mL, 13.7 mmol). The stirred mixture

was allowed to warm slowly to room temperature. A white precipitate formed. The solvent was removed under vacuum, the precipitate was dried, and 50 mL of dry toluene and 2 mL of P(SiMe₃)₃ (6.87 mmol) were added. The mixture was heated to reflux for 8 h, during which time the colour turned pale-yellow. Removal of volatiles afforded a pale-yellow residue which was extracted with dry toluene (4 \times 20 mL). The combined extracts were reduced to ~15 mL. Cooling to -25 °C gave large colourless crystals of 1 (1.42 g, 1.5 mmol, 43.7%), m.p. 209 °C (decomp.). ¹H NMR (300 MHz, CD₂Cl₂): δ 7.07 (m, 4H, *m*-Ph), 6.87 (m, 6H, o- and p-Ph), 2.33 (s, 4H, CH₂), 0.32 (t, 18H, SiMe₃, $J_{\rm HP} = 5.6$ Hz). ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz): δ 146.27 (Ph, ipso-C), 129.46, 128, 68 (Ph, o-C, m-C), 122.72 (Ph, p-C), 25.75 (t, $J_{CP} = 17.4$ Hz, CH₂), 4.58 (t, $J_{CP} = 9.3$ Hz, SiMe₃). ³¹P NMR (121.5 Hz, CD₂Cl₂): δ –220.3. Anal. Found: C, 51.05; H, 7.06. Calcd for C₂₀H₃₂InPSi₂: C, 50.63; H, 6.80%.

Representative procedure for the synthesis of InP nanowires

All operations are conducted under dry nitrogen. A 100 mL 3neck flask, equipped with a reflux condenser, septum and a temperature sensor probe was charged with 10 mL of methyl myristate and the contents heated to 310 °C. Then a solution of 1 in diphenyl ether (0.02 M, 1.6 mL, 0.03 mmol w.r.t. In) was injected as quickly as possible through the rubber septum, with vigorous stirring. Instantly a black precipitate was formed. The temperature control was set to 250 °C, the solution was stirred for 10 min at 250 °C and then cooled to room temperature. For injection temperatures below 250 °C, the growth temperature was kept constant at 160 °C for all samples. The black precipitate was centrifuged, washed several times with toluene and dispersed in dichloromethane.

Removal of the indium metal tip

The nanofibres synthesized as above were dispersed in 10 mL of methyl myristate and placed into a 100 mL 3-neck flask equipped with a reflux condenser, septum and a temperature sensor probe. To this was added $P(SiMe_3)_3$ (1 mL, 3.43 mmol). The contents was heated to 250 °C by a temperature controlled heating mantle, and thiophenol was injected (1.1 mL, 10.3 mmol). The mixture was kept at 250 °C for 30 min with continuous stirring. After cooling to room temperature the black precipitate was centrifuged, washed several times with toluene and dispersed in dichloromethane.

Crystal structure determination of complex 1

A crystal of **1** was examined at 140(1) K on an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer, equipped with Mo-K α radiation and graphite monochromator. Intensity data were measured by thin-slice ω - and φ -scans. Data were processed using the CrysAlisPro-CCD and -RED²⁷ programs. The structure was determined by the direct methods routines in the SHELXS program²⁸ and refined by full-matrix least-squares methods, on F^2 's, in SHELXL.²⁸ The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions and their $U_{\rm iso}$ values were set to ride on the $U_{\rm eq}$ values of the parent carbon atoms. Computer programs used in this analysis have been noted above, and were run through WinGX.²⁹ *Crystal data*: C₄₀H₆₄In₂P₂Si₄, M = 948.85, triclinic, space group $P\bar{1}$ (no. 2), Z = 1, a = 10.6674(9), b = 10.7597(2), c = 12.1674(12) Å, $\alpha = 102.721(9)$, $\beta = 113.424(5)$, $\gamma = 106.954$ (1)°, U = 1132.32(15) Å³, T = 140 K, 23 201 reflections measured, 6588 unique ($R_{\rm int} = 0.034$) which were used in all calculations. The final w R_2 was 0.053 (all data).

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