The Reaction of Indium(III) chloride with Tris(trimethylsilyl)phosphine: A Novel Route to Indium Phosphide

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InP has been prepared by the reaction of $InCl_3$ with $P(SiMe_3)_3$; the intermediates and product have been characterised by *X*-ray photoelectron spectroscopy, elemental analysis, and *X*-ray powder diffraction.

The technological importance of the III–V semiconductor compounds, GaAs and InP, has led to a renewed interest in the chemistry of compounds containing covalent bonds between the heavier group III and V elements.[1] One such class of compounds with empirical formula $(R_2MER'_2)_n$ (M = Ga, In; E = P, As) is prepared by the reaction of a gallium or indium trialkyl compound with a secondary phosphine or arsine (equation 1).[2] This reaction has been used as the basis for the synthesis of semiconductor thin films by metallo-organic chemical vapour deposition (MOCVD) (equation 2).[3] Wells *et al.*[4] have shown that trimethylsilyl substituted arsines will react cleanly with gallium halides, at low temperatures, to yield covalent Ga–As bonds, and trimethylsilyl halide (equation 3). We have applied this 'silyl methodology' to the formation of In–P bonds (equation 4).[5]

$$MR_3 + HER'_2 \rightarrow R_2MER'_2 + RH \qquad (1)$$

$$MR_3 + EH_3 \rightarrow (ME)_n + 3RH \qquad (2)$$

$$M = Ga, In \quad E = P, As$$

$$2GaCl_3 + 4(Me_3SiCH_2)_2As(SiMe_3) \rightarrow \{[(Me_3SiCH_2)_2As]_2GaCl\}_2 + 4Me_3SiCl \qquad (3)$$

$$2Me_2InCl + 2Ph_2P(SiMe_3) \rightarrow (Me_2InPPh_2)_2 + 2Me_3SiCl \qquad (4)$$

The relatively mild conditions required for these reactions, often below room temperature, have prompted us to investigate the use of $P(SiMe_3)_3$ for the preparation of polycrystalline indium phosphide.

Addition of $P(SiMe_3)_3$[6] (5% excess) to a toluene suspension of $InCl_3$ at −78 °C resulted in the formation of a pale yellow solid. As the reaction was warmed to room temperature the solid darkened. Removal of all volatiles by distillation (10^{-2} Torr) yielded a bright orange powder (**1**), which was insoluble in organic solvents but reacted with inorganic mineral acids to liberate phosphine. Based on *X*-ray photoelectron spectroscopy (XPS) and elemental analysis† we propose this orange powder to be an oligomer $[Cl_2InP(SiMe_3)_2]_x$ (**1**).

Heating (**1**) at 150 °C for 2 h (*in vacuo*) gave a dark brown powder (**2**). The elimination of Me_3SiCl was confirmed by g.c. Although the molecular formula of (**2**) is $[InClP(SiMe_3)]_x$, the XPS spectrum† indicates the presence of two environments for both indium and phosphorus. One set of peaks ($3d_{5/2}$ and $3d_{3/2}$) is similar to those found for (**1**), while the other set resemble those found for InP [Figure 1 shows the high resolution spectra in the In 3d region for (**1**) and (**2**)]. The *X*-ray powder diffraction shows no InP formation, indicating that (**2**) is not a mixture of polycrystalline InP and (**1**). We propose (**2**) to be $\{(InCl_2)[P(SiMe_3)_2](In)(P)\}_x$ which is

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† XPS Spectra were collected on a Surface Science Instruments Spectrometer (Model SSX-100) with a monochromatised Al-K_α source. The spectra were acquired with a 100 eV pass energy and 600 µm spot. Radiation damage was insigificant over the acquisition times used.

Compound (**1**): XPS, eV (%); P 2p, 125.7; Cl 2p, 194.9(60), 196.5(40); In $3d_{5/2}$, 441.6; In $3d_{3/2}$, 449.1. Atomic ratio In : P : Cl; 1 : 1 : 2. Anal. calcd. for $C_6H_{18}Cl_2InPSi_2$: C, 19.8; H, 4.99; Cl, 19.5; P, 8.52. Found: C, 20.0; H, 5.02; Cl, 19.3; P, 8.51.

Compound (**2**): XPS, eV (%); P 2p, 125.7(48), 129.4(52); Cl 2p, 194.8(58), 196.5(42); In $3d_{5/2}$, 441.3(48), 444.1(52); In $3d_{3/2}$, 449.1(48), 452.0(52). Atomic ratio In : P : Cl; 1 : 1 : 1. Anal. calcd. for $C_3H_9ClInPSi$: C, 14.2; H, 3.56: Cl, 13.9; P, 12.2. Found: C, 14.1; H, 3.61; Cl, 13.5; P, 12.1.

Compound (**3**): XPS, eV (%); P 2p, 128.4; In$3d_{5/2}$, 444.9; In $3d_{3/2}$ 452.9. Atomic ratio In: P; 1 : 1. Anal. calcd. for InP: P, 21.2. Found: P, 20.9: C, 0.1.

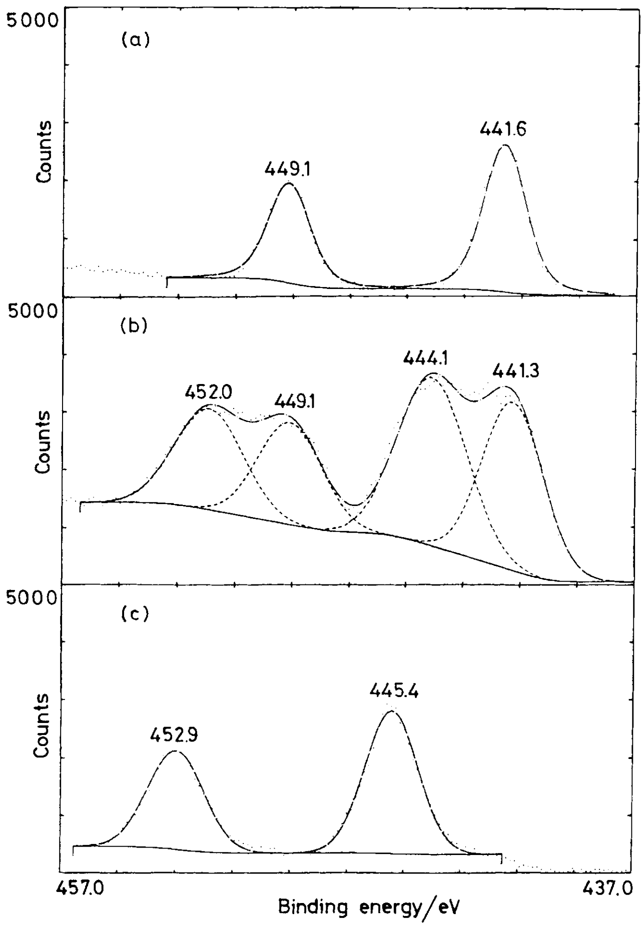

Figure 1. In 3d, curve fitted XPS spectral components for compounds (**1**)(a), (**2**)(b), and (**3**) (InP)(c). Peak positions are included (eV).

consistent with the XPS and analytical data. Like (**1**), (**2**) is insoluble in organic solvents and liberates phosphine on reaction with acids.

On heating (**2**) at 650 °C for 1 h, under vacuum, the last equivalent of Me_3SiCl was removed to yield InP (**3**), as a black powder. Chlorine and silicon could not be detected by XPS and analytical data.‡ XPS Peaks due to O and C are observed in addition to peaks due to the In and P and are possibly due to the native oxide and some inadvertent carbon contamination due to air exposure.[7] The *X*-ray powder diffraction confirms the product to be primarily polycrystalline indium phosphide.§

Preliminary results show that InP of equal purity can be synthesised using $InBr_3$ as the indium source, however, the use of InI_3 results in iodine incorporation into the InP produced. It is interesting to note, however, that no Si, an n-type dopant, could be detected by XPS. Compounds (**1**) and (**2**) are not sufficiently volatile to be used as precursors for MOCVD, however, we are exploring the possible use of the $InCl_3/P(SiMe_3)_3$ systems for the growth of InP thin films.

Note: While this manuscript was in preparation, Professor R. L. Wells communicated to us results of the preparation of GaAs by the reaction of $GaCl_3$ with $As(SiMe_3)_3$.

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‡ XPS is not sufficiently sensitive to determine whether the amounts of Si remaining are significant for use of InP as a semiconductor. The purity needed for semiconductor applications is less than 1 part in 10^{10}.

§ The *X*-ray powder diffraction pattern was confirmed as InP by comparison with an authentic sample.