Synthesis and purification of some main group organometallic precursors for compound semiconductors

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Abstract. Metal–organic vapour phase epitaxy/chemical vapour deposition (MOVPE/MOCVD) has emerged recently as the method of choice for large scale preparation of a variety of low dimension inorganic materials; particularly compound semiconductors, used in modern electronic and opto-electronic devices. The success of this process depends on the availability of suitable molecular precursors of desired purity. Group V hydrides (e.g. NH_3 , PH_3 , AsH_3 , SbH_3) have been employed conventionally for deposition of III–V semiconductor materials. Inherent weakness of this hydride source, particularly heavier ones (for instance very low utilization (> 0.1%) of AsH_3 in GaAs synthesis; ~ 4 h half life of SbH_3 at room temperature) has been a driving force to develop new molecular precursors with desirable properties. This talk will briefly review synthesis and purification of several precursors of groups III (Ga, In), IV, V (As, Sb) and VI (Se, Te).

Keywords. Tertiary arsines; triorganoantimony; palladium(II); TGA.

1. Introduction

Since the first demonstration of GaAs growth by MOCVD in 1968 (Manasevit 1968; Manasevit and Simpson 1969), extensive work on synthesis of various inorganic materials by CVD techniques has been carried out particularly during the last fifteen years. These techniques employ metallo–organic compounds which are required in high purity. As the complexity of electronic devices is increasing with time, the demand for low decomposition temperature metallo–organic precursors with cleaner deposition is also growing. At BARC, we have carried out synthesis of conventional as well as new precursors and have also developed methods for their purification. To maintain a high level of purity consistently, we have adopted adduct purification method for organometallic compounds. A relatively non-volatile adduct is easy to handle and can be purified by recrystallization. The adduct is prepared by combining an appropriate Lewis base (electron rich compound) with a Lewis acid (electron deficient compound). Thermal dissociation of these adducts at an appropriate temperature generates pure organometallic compound which can be obtained as and when required. Group wise synthetic and purification approach is described here.

2. Organo-gallium and -indium compounds

Organo-gallium and -indium compounds, particularly trimethyl and -ethyl, are extensively used for deposition of III–V materials by chemical vapour deposition methods. Several routes (1–8) are known to prepare these compounds (Dennis and Pantode 1932; Renwanz 1932;

Wiberg *et al* 1943; Coates 1951; Runger *et al* 1951; Bregadze *et al* 1973; Gaines *et al* 1974; Kovar *et al* 1975; Jones *et al* 1983, 1984; Ninomiya *et al* 1990; Bhatt *et al* 2002), each of them having its own advantages and limitations,

Organo-gallium and -indium compounds are obtained by the reactions of magnesium alloys with alkyl iodide in diethyl ether (7 and 8). The reaction with gallium–magnesium alloys are quite facile, but the corresponding reactions with indium alloys are very sluggish and require several hours (12–16 h) for completion. Best yields are obtained from homogeneous phase of Mg_5Ga_2 . Inhomogeneous alloys often lead to the formation of Grignard reagent and gallium metal. Although diethyl ether adduct of R_3Ga is quite useful for a variety of chemical reactions (Prasad *et al* 2002; Kushwah *et al* 2004), the adduct free

Table 1. Boiling point of organo-gallium and -indium compounds.

Compound	B.P. Diethylether adduct	B.P. Base free
Trimethylgallium	98–99°C/760 mm	56°C/760 mm
Triethylgallium	30°C/3 mm	143°C/760 mm
Trimethylindium	110–120°C	66–67°C/12 mm
Triethylindium	65°C/30 mm	83–84°C/12 mm

alkyl (table 1) is obtained by coordinating with diphenylether, liberated diethyl ether is distilled off and the diphenylether adduct so formed, on pyrolysis affords base free trialkyl gallium compounds (Khatkhate *et al* 1990).

3. Organo-arsenic and -antimony compounds

In order to replace conventional group V precursors (AsH_3 and SbH_3) due to their inherent weakness, extensive work is being carried out to design and develop suitable molecules with desirable properties. We have synthesized several organo-arsenic and -antimony compounds and these are summarized in table 2. These compounds are readily prepared by the reactions of a suitable metal halide with Grignard reagent in diethylether or tetrahydrofuran (9–11) (Garje *et al* 1999; Chaudhari *et al* 2002, 2003; Phadnis *et al* 2002a,b, 2003a,b; Mahalakshmi *et al* 2003a,b).

These compounds are readily purified by distillation (liquids) under a reduced pressure or by recrystallization (solids) from petroleum ether/hexane. They were characterized by NMR spectroscopy which showed expected resonances. The alkylarsines and stibines form various complexes with palladium and platinum salts. The complexes of the type $[\text{MCl}_2(\text{ER}_3)_2]$, isolated by the reaction of $[\text{MCl}_2(\text{MeCN})_2]$ with ER_3 in dichloromethane, are of particular interest. These complexes are readily recrystallized to a high degree of purity from appropriate solvents and on thermolysis release coordinated trialkylarsine as revealed by TG analysis (figure 1). Thus this method is advantageous not only in storing air sensitive compounds as stable adducts but also in purifying the precursor conveniently.

The X-ray structures of $(\text{C}_6\text{F}_5)_3\text{E}$ (E = As, Sb, Bi) revealed that metal is in a trigonal pyramidal configuration. Coordination around arsenic or antimony in palladium and platinum complexes approaches nearly tetrahedral configuration (figure 2).

4. Precursors for V–VI materials

Group V chalcogenides of the type E_2Ch_3 (E = As, Sb,

Figure 1. TG curves of $[\text{PdCl}_2(\text{AsR}_3)_2]$.

Bi; Ch = S, Se, Te) are semiconductors with a band gap varying between 2.36 (As_2S_3) and 0.15 (Bi_2Te_3) eV and find several applications such as halographic recording, thermoelectric coolant, etc. Complexes of chelating chalcogenolate ligands offer a promising alternative as they

Figure 2. Structures of palladium adducts.

can deliver both metal and chalcogen in the same molecule. These complexes are usually significantly more stable, less toxic, non-pyrophoric and easier to handle than their alkyl derivatives (Bochmann 1996).

Keeping this in mind organo-arsenic, -antimony and -bismuth compounds with xanthates, dithiocarbamates and dithiophosphates have been synthesized employing the following reaction route (12). This work has been reviewed recently (Garje and Jain 2003).

These complexes have been characterized by elemental analysis, IR, NMR (^1H , ^{13}C , ^{31}P), mass spectra and X-ray (figure 3) structural analyses (Garje *et al* 1997; Garje and Jain 2003; Gupta *et al* 2003). The xanthate complexes tend to decompose on slight heating as revealed by TG analysis. The mass spectra did not show molecular ion peaks for xanthate complexes. Thus methylbismuth com-

Table 2. Boiling and melting points of organo-arsenic, -antimony and -bismuth compounds.

Compound	Nature	M.P./B.P.
$\text{Pr}_3^{\text{n}}\text{As}$	colourless liquid	50–55°C/3 mm
$\text{Pr}_3^{\text{i}}\text{As}^*$	colourless liquid	49–56°C/3 mm
$(\text{CH}_2=\text{CHCH}_2)_3\text{As}^*$	colourless liquid	52–53°C/2.5 mm
$(\text{CH}_2=\text{C}(\text{Me})\text{CH}_2)_3\text{As}^*$	colourless liquid	53–55°C/2.5 mm
$\text{Bu}_3^{\text{n}}\text{As}$	colourless liquid	105–109°C/9 mm
$\text{Bu}_3^{\text{i}}\text{As}$	colourless liquid	150–155°C/100 mm
$\text{Bu}_3^{\text{s}}\text{As}$	colourless liquid	100–103°C/9 mm
$\text{Bu}_3^{\text{t}}\text{As}$	colourless liquid	75–80°C/9 mm
$\text{Me}_2\text{As}(\text{CH}_2\text{C}_6\text{H}_5)^*$	colourless liquid	44–45°C/2 mm
$\text{PhAs}(\text{CH}_2)_5^*$	colourless liquid	115–120°C/2.5 mm
$(\text{C}_6\text{F}_5)_3\text{As}^{**}$	colourless liquid	112°C
$(\text{C}_4\text{H}_9\text{S})_3\text{As}$	pale yellow oil	150–160°C/0.4 mm
$\text{Pr}_3^{\text{n}}\text{Sb}$	colourless liquid	50–52°C/3 mm
$\text{Pr}_3^{\text{i}}\text{Sb}^*$	colourless liquid	48°C/3 mm
$\text{Bu}_3^{\text{n}}\text{Sb}$	colourless liquid	70–85°C/3–4 mm
$\text{Bu}_3^{\text{i}}\text{Sb}$	colourless liquid	85–90°C/3–4 mm
$\text{Bu}_3^{\text{s}}\text{Sb}$	colourless liquid	80–90°C/3–4 mm
$\text{Bu}_3^{\text{t}}\text{Sb}$	pale yellow liquid	90–100°C/3–4 mm
$(\text{CH}_2=\text{CHCH}_2)_3\text{Sb}$	colourless liquid	70–73°C/2 mm
$(\text{CH}_2=\text{CMeCH}_2)_3\text{Sb}$	colourless liquid	68–70°C/2 mm
$(\text{C}_4\text{H}_9\text{S})_3\text{Sb}$	off white crystals	45°C
$(\text{C}_6\text{F}_5)_3\text{Sb}^{**}$	colourless crystals	76°C
$(\text{C}_6\text{F}_5)_3\text{Bi}^{**}$	colourless crystals	

*Structures established by X-ray crystallography as their palladium(II) adducts; **structures established by X-ray crystallography.

Figure 3. X-ray structures of methyl-arsenic and -bismuth compounds.

Figure 4. XRD pattern for Bi_2S_3 .

plexes $[\text{MeBi}(\text{S}_2\text{COR})_2]$ in refluxing xylene afforded pure Bi_2S_3 (figure 4) (Gupta *et al* 2003).

5. Organoselenium and tellurium compounds

Organoselenium and tellurium compounds have been prepared by the reactions of sodium/potassium chalcogenides with alkylhalides (Dey *et al* 2001, 2003). Both mono- and di-chalcogenides are successfully used for the synthesis of a variety of metal chalcogenides.

6. Conclusions

This work demonstrates convenient methods for purification of groups III and V organometallic compounds. Metal chalcogenides are readily obtained from simple molecular precursors which have also been used for the preparation of nano particles of metal chalcogenides.

Acknowledgements

The author sincerely thanks all his collaborators and Ph.D. students whose names appear in references for their enthusiasm in this work. Drs T Mukherjee and S K Kulshreshtha are thanked for encouragement.

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