

JOM 23374

## Antimony sources for MOCVD. The use of $\text{Et}_4\text{Sb}_2$ as a p-type dopant for $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ and crystal structure of the adduct $[\text{Et}_4\text{Sb}_2 \cdot 2\text{CdI}_2]_n$

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(Received August 3, 1992)

### Abstract

Tetraethyldistibine,  $\text{Et}_4\text{Sb}_2$ , a new antimony source for MOCVD is evaluated. It is shown to be a useful and safe dopant feedstock for low temperature growth of p-type  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ . Attempted purification of  $\text{Et}_4\text{Sb}_2$  by adduct formation with  $\text{CdI}_2$  resulted in isolation of a polymeric chain adduct  $[\text{Et}_4\text{Sb}_2 \cdot 2\text{CdI}_2]_n$  (1). The structure of 1 has been determined by X-ray crystallography and consists of chains of iodide-bridged  $\text{Et}_4\text{Sb}_2 \cdot 2\text{CdI}_2$  units which have  $\text{CdI}_2$  bonded to each antimony atom. Antimony and two iodine atoms form a trigonal planar arrangement around cadmium, and two weak axial bonds to the iodine atoms of adjacent units give distorted trigonal bipyramidal coordination to cadmium. The distibine molecules display a skew configuration of the ethyl substituents. The  $\text{Sb}^{\text{II}}-\text{Sb}^{\text{II}}$  and  $\text{Sb}^{\text{II}}-\text{Cd}^{\text{II}}$  distances are 2.784(2) and 2.822(2) Å respectively. Dropwise addition of  $\text{Me}_2\text{Cd}$  to  $\text{Et}_4\text{Sb}_2$  in the absence of solvent gave an insoluble 1:1 adduct.  $\text{Et}_4\text{Sb}_2$  reacts with Te but not with Cd or Hg.

### 1. Introduction

Deposition of antimony thin films is the focus of intense research interest. The metal film is useful in preparing decorative and anti-corrosion coatings, as well as mirrors and electrical contacts. Numerous antimony alloys are also desired as thin films. These include  $\text{Sb}_2\text{Te}_3$  which is used in thermoelectric and rewritable optical recording materials, and InSb which is an important infrared detector material.

One of the most powerful methods for growth of many antimony containing materials is Metal Organic Chemical Vapour Deposition (MOCVD). Successful application of this process is largely dependent on the availability and properties of suitable source organometallics. MOCVD is also applied to the growth of other alloys including  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  (MCT).

Control of the electrical properties of MCT is a current goal in the development of advanced optoelectronic devices. The manipulation of the cation vacancy

defect concentration by adjustment of growth stoichiometry and annealing conditions can allow production of n-type or p-type material. However many devices require low defect levels and thin films incorporating carefully graded junctions. Extrinsic doping of bulk and epitaxial MCT has been intensively investigated as discussed in a recent comprehensive review [1]. Growth at low temperature and under conditions where stoichiometry can be controlled will enable production of high performance devices.

There is particular interest in production of extrinsic p-type MCT because it yields superior photoconductors for room temperature operation [2]. Achievement of p-type dopant activity has proven to be difficult. Group 1 elements are fast diffusers leading to unstable junctions. Segregation of some elements from bulk and LPE material has limited the incorporation of some potential p-dopants. The Group 15 elements also exhibit amphoteric behaviour with a tendency to sit on cation sites in material grown from tellurium-rich melts [3,4]. Conventional MBE with Sb metal has yielded n-type material [5] although photo-assisted MBE with Sb gives p-type MCT [6,7]. Arsenic and antimony are promising dopants if they can be activated on the

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tellurium sites. Both are slow diffusers with reported estimates of diffusion coefficients  $D_{As} = 1-20 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$  for  $x < 0.5$  at 410°C [8] and  $D_{Sb} = 1.3 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$  for  $x = 1.0$  at 300°C [9].

For mass production of sophisticated devices, MOCVD of p-type MCT would be preferable to other growth techniques. There have been reports by three research groups on the use of arsine for deliberate extrinsic doping of CdTe [10–12] and MCT [8,13–18]. When the interdiffused multilayer process (IMP) [19] was used, arsenic was found to be incorporated only in the CdTe layers. The growth also occurred at temperatures well below that normally required to achieve significant cracking of the arsine, and high arsine flow led to reduction of the cadmium fraction in the layers. This implies that there is a reaction between the dimethylcadmium and arsine, potentially causing gas-phase nucleation and thus limiting the utility of arsine. Successful doping with phosphine has also been reported [15,20]. The extreme toxicity of arsine and phosphine, their high thermal stabilities, the tendency to pre-reaction with dimethylcadmium, and the need to use high-pressure gas cylinders with the active gases diluted in order to give controllable low-level dopant delivery, make these gases undesirable feedstocks for MOCVD doping of MCT.

The low diffusion coefficient for arsenic at the MOCVD growth temperatures will lead to uneven distribution of the dopant throughout an IMP grown layer, requiring extended high-temperature annealing to homogenise the layer. It would be desirable to find a p-type dopant source which could be incorporated in both the HgTe and CdTe layers. Attempts at p-doping of MCT using organometallics of the Group 15 elements have been reported [21,22]. Using trimethylarsine ( $\text{Me}_3\text{As}$ ), less than 0.01% of the available arsenic was incorporated or electrically active in MCT grown at 410°C [21], consistent with the high thermal stability of  $\text{Me}_3\text{As}$  [23]. When trimethylstibine ( $\text{Me}_3\text{Sb}$ ) was used, p-type material was obtained but the cadmium fraction of the layers was reduced and poor surface morphologies were observed [21]. As discussed in a recent review of organometallics for MOCVD of MCT [24], the methyl derivatives of Group 15 elements are too volatile to allow controlled doping levels using the bubbler delivery mode, and the strong element–methyl bond is anticipated to lead to extensive carbon contamination of the epilayers. The onset temperature for pyrolysis of  $\text{Me}_3\text{Sb}$  in a hydrogen stream is reported [25] to be 375°C, with 100% pyrolysis occurring at 450°C. In a fluidised bed [26], onset of pyrolysis is at 475°C, but in a vacuum [27] cracking temperatures of higher than 800°C had to be used. The triethyl derivatives  $\text{Et}_3\text{E}$  (E = As, Sb, Bi) have been evaluated for

MOCVD applications with the decomposition temperature decreasing down the group [28]. As might be expected, these larger molecules have considerably lower vapour pressures (6.2 and 2.9 mm Hg for  $\text{Et}_3\text{As}$  and  $\text{Et}_3\text{Sb}$  respectively at 20°C) than the methyl compounds [4]. These vapour pressures are still relatively high for the purpose of introducing dopant levels of the elements.

Recently, growth of InSb at temperatures around 350°C was achieved with triisopropylstibine [29], which has a vapour pressure of 0.3 mm Hg at 16.5°C. Investigation of other antimony sources with bulky ligands such as neopentyl or trimethylsilylmethyl has been reported [30], but it has been pointed out that bulky ligands might actually stabilise the metal–carbon bond because the transmission of energy to the metal atom might be slow within the collisionally energised molecule [31]. A trimeric single source compound for InSb growth,  $[\text{Me}_2\text{InSb}(\text{t-Bu})_2]_3$ , proved unsatisfactory for low temperature growth, requiring a substrate temperature of 450°C and an unacceptable source temperature of 125°C [32].

In summary a suitable p-type dopant for MOCVD of MCT and related materials should have the following characteristics: (i) a low decomposition temperature, (ii) no appreciable pre-reaction in the gas phase with other reagents, (iii) decomposition without retention of carbon, (iv) preferably be a liquid so that the conventional bubbler source container can be used, and (v) a sufficiently low vapour pressure between 0°C and ambient temperatures that it can be used with standard mass flow controllers to give a wide range of dopant atom concentrations. In addition, the dopant atom should have a low interdiffusion coefficient at the growth temperature.

Here we report low temperature extrinsic doping in MCT by the successful use of tetraethylstibine ( $\text{Et}_4\text{Sb}_2$ ), which fulfils all the requirements mentioned above. The crystal structure of the  $\text{CdI}_2$  adduct of the antimony source is presented. We also discuss some reactions of  $\text{Et}_4\text{Sb}_2$  with tellurium and tellurium alkyls relevant to its use in MOCVD growth of antimony doped MCT.

## 2. Experimental section

### 2.1. General procedures

All reactions were carried out under dry oxygen-free argon, using standard Schlenk techniques. Solvents were purified according to literature methods [33] and distilled from sodium and benzophenone prior to use. Dimethylcadmium was obtained by the method of Anderson and Austin [34]. The 2,2'-bipyridine adduct was prepared by reacting an excess of 2,2'-bipyridine with

dimethylcadmium in diethyl ether [35]. Magnesium turnings and tellurium powder were stirred under vacuum at 200°C for 12 h before use. Antimony trichloride and tellurium powder were obtained from Aldrich Chemical Company, Wisconsin, USA.

Nuclear Magnetic Resonance spectra were recorded on a Bruker AC-200 spectrometer. All NMR spectra were recorded in deuterated benzene, the C<sub>6</sub>H<sub>6</sub> peak ( $\delta$  7.15 ppm for <sup>1</sup>H and 128.0 ppm for <sup>13</sup>C) was used as an internal reference. <sup>125</sup>Te chemical shifts are reported upfield from the external reference TeMe<sub>2</sub>. Mass spectra were recorded on a VG TRIO-1 GC-MS instrument. Only major and/or structurally significant peaks are reported. Vapour pressures were calculated from mass loss recorded on a Cahn R100 series Microbalance using the Knudsen Effusion method [36,37].

The samples for EDX and XPS spectroscopy were initially analysed in a Cambridge Instruments S360 electron microscope, utilising Secondary Electron Imaging (SEI), Back-Scattered Electron Imaging (BEI) and Ultra-Thin Window Energy Dispersive X-ray (UTW-EDX) analysis. The primary electron beam was operated over the range of 10–20 keV, with a beam current of 200 pA. The XPS data were obtained using a Vacuum Generators (VG) HB-100 electron spectrometer, which operates at a base pressure of better than 10<sup>-10</sup> mbar. A VG AG-60 ion gun was used to produce argon ions which were employed to clean away surface contaminants. X-rays were generated by a dual-anode (Mg/Al) source, utilizing the Al K $\alpha$  line (1486.6 eV), which was operated at 15 kV and 32 mA. The resulting photoelectrons were analysed via a VG CLAM-100 150° spherical sector electrostatic analyser, which was operated in the constant analyser energy (CAE) mode with a pass energy of 50 eV. The data collection and processing were performed by a DEC 11/23 minicomputer.

Microanalyses for C and H were carried out by the National Analytical Laboratories Pty. Ltd., Victoria, Australia.

### 2.2. Preparation of tetraethylstibine, Et<sub>4</sub>Sb<sub>2</sub>

Et<sub>3</sub>Sb was obtained by reaction of the Grignard reagent EtMgI, with SbCl<sub>3</sub> in diethyl ether at 0°C [38]. Yields of 80–90% were generally obtained. Et<sub>3</sub>SbBr<sub>2</sub> was formed in 98% yield by dropwise addition of bromine to Et<sub>3</sub>Sb in diethyl ether at 0°C [39]. Et<sub>2</sub>SbBr was produced by the thermal decomposition of Et<sub>3</sub>SbBr<sub>2</sub> at 190°C and 400 mm Hg for 30 min [39]; it was purified by distillation at 50°C under dynamic vacuum conditions. The yield was 75%. To Mg turnings in THF was added one molar equivalent of Et<sub>2</sub>SbBr. The exothermic reaction caused the solvent to reflux gently. The solution was left to stir at ambient temper-

ature for approximately twelve hours. Solvent was removed under vacuum and the residue extracted four times with small portions of pentane. Subsequent removal of pentane yielded a yellow thermochromic liquid [40]. The yield of Et<sub>4</sub>Sb<sub>2</sub> was 82%. In a typical preparation, about 10 g of the product was obtained. Et<sub>4</sub>Sb<sub>2</sub> is a light sensitive compound which should be stored in the dark. Anal. Found: C, 26.6; H, 5.6. C<sub>8</sub>H<sub>20</sub>Sb<sub>2</sub> calc.: C, 26.7; H, 5.6%. <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.62 (m, ABX<sub>3</sub> system, 8H, CH<sub>2</sub>), 1.32 (pseudo-triplet, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR spectrum (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.20 (s, CH<sub>2</sub>), 14.96 (s, CH<sub>3</sub>). Mass spectrum: 360 (100%, M), 331 (28%, M – Et), 303 (70%, Sb<sub>2</sub>Et<sub>2</sub>H<sup>+</sup>), 275 (62%, SbEtH<sub>2</sub><sup>+</sup>), 273 (48%, M – 3Et), 245 (30%, Sb<sub>2</sub>H<sup>+</sup>), 244 (25%, Sb<sub>2</sub><sup>+</sup>), 179 (15%, SbEt<sub>2</sub><sup>+</sup>), 151 (33%, SbEtH<sup>+</sup>), 149 (28%, SbC<sub>2</sub>H<sub>4</sub><sup>+</sup>), 121 (18%, Sb<sup>+</sup>). Vapour pressure: 0.006 mmHg at 18°C. Decomposition at 300°C in a H<sub>2</sub> atmosphere gave a thin film of antimony metal (no impurities evident from XPS analysis).

### 2.3. Preparation of tetramethyldistibine, Me<sub>4</sub>Sb<sub>2</sub>

Me<sub>4</sub>Sb<sub>2</sub> was prepared in similar manner [40], except that Me<sub>3</sub>SbBr<sub>2</sub> was decomposed at 200°C and 100 mm Hg [41]. Me<sub>4</sub>Sb<sub>2</sub> is a yellow thermochromic liquid (mp 17°C) [40] and was obtained in 71% yield. It was purified by distillation at 50°C and 0.05 mm Hg. <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.84 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR spectrum (C<sub>6</sub>D<sub>6</sub>):  $\delta$  –10.98 (s, CH<sub>3</sub>). Mass spectrum: 304 (55%, M), 289 (42%, M – Me), 274 (28%, M – 2Me), 273 (14%, SbMeCH<sub>2</sub><sup>+</sup>), 259 (35%, M – 3Me), 245 (12%, Sb<sub>2</sub>H<sup>+</sup>), 244 (22%, Sb<sub>2</sub><sup>+</sup>), 151 (100%, SbMe<sub>2</sub><sup>+</sup>), 136 (27%, SbMe<sup>+</sup>), 121 (21%, Sb<sup>+</sup>). Decomposition at 300°C in a H<sub>2</sub> atmosphere gave a thin film of antimony metal (XPS analysis).

### 2.4. Reaction of Et<sub>4</sub>Sb<sub>2</sub> with Te

Et<sub>4</sub>Sb<sub>2</sub> was added to one equivalent of Te powder. After 30 min, the yellow suspension had turned red. After a further 4 h, pentane was added to the mixture. The solution was filtered and solvent removed under vacuum to give the red liquid Et<sub>2</sub>SbTeSbEt<sub>2</sub> [42] in a yield of 82%. <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.67 (m, ABX<sub>3</sub> system, 8H, CH<sub>2</sub>), 1.31 (pseudo-triplet, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR spectrum (C<sub>6</sub>D<sub>6</sub>):  $\delta$  13.60 (s, CH<sub>3</sub>), 7.71 (s, CH<sub>2</sub>). <sup>125</sup>Te NMR spectrum:  $\delta$  –725.7. Mass spectrum: 488 (28%, M), 459 (82%, M – Et), 431 (18%, Sb<sub>2</sub>TeEtH<sup>+</sup>), 430 (26%, M – 2Et), 401 (100%, M – 3Et), 373 (46%, Sb<sub>2</sub>TeH<sup>+</sup>), 372 (58%, M – 4Et), 360 (18%, M – Te), 309 (14%, SbTeEt<sub>2</sub><sup>+</sup>), 303 (18%, Sb<sub>2</sub>Et<sub>2</sub>H<sup>+</sup>), 281 (38%, SbTeEtH<sup>+</sup>), 273 (36%, Sb<sub>2</sub>Et<sup>+</sup>), 251 (94%, SbTe<sup>+</sup>), 244 (32%, Sb<sub>2</sub><sup>+</sup>), 179 (18%, SbEt<sub>2</sub><sup>+</sup>), 151 (62%, SbEtH<sup>+</sup>), 149 (62%, SbC<sub>2</sub>H<sub>4</sub><sup>+</sup>), 121 (40%, Sb<sup>+</sup>).

### 2.5. Reaction of *Et<sub>4</sub>Sb<sub>2</sub>* with *Et<sub>2</sub>Te*

*Et<sub>2</sub>Te* was added dropwise to one equivalent of *Et<sub>4</sub>Sb<sub>2</sub>* at 0°C. No immediate reaction was observed. NMR spectra of the yellow/orange solution showed that it contained a mixture of compounds. The major components were the two starting materials; some *Et<sub>3</sub>Sb* and smaller amounts of *Et<sub>2</sub>SbTeEt* and *Et<sub>2</sub>SbTeSbEt<sub>2</sub>* were also present.

### 2.6. Reaction of *Et<sub>4</sub>Sb<sub>2</sub>* with *Me<sub>2</sub>Cd*

*Me<sub>2</sub>Cd* was added dropwise to *Et<sub>4</sub>Sb<sub>2</sub>*. An immediate red/brown precipitate formed; it was washed several times with pentane to remove any unchanged starting materials. The precipitate is air sensitive and is not soluble in any common organic solvents. Anal. Found: C, 24.0; H, 5.1. *Me<sub>2</sub>Cd*:*Sb<sub>2</sub>Et<sub>4</sub>* calcd.: C, 23.9; H, 5.2%.

### 2.7. Treatment of *Et<sub>4</sub>Sb<sub>2</sub>* with *Hg* and *Cd*

Neat *Et<sub>4</sub>Sb<sub>2</sub>* was added to samples of *Hg* and *Cd* in separate Schlenk flasks. The contents of the flasks were stirred, and subsequently placed in an ultrasound bath. No reaction was evident from the NMR spectra, even after prolonged reaction times.

### 2.8. Attempted adduct purification of *Et<sub>4</sub>Sb<sub>2</sub>*

*CdI<sub>2</sub>* dissolved in THF was added dropwise to a solution of *Et<sub>4</sub>Sb<sub>2</sub>* in THF. There was no immediate colour change. The reaction mixture was placed in the dark for about a week. After this time, the solvent was removed under vacuum to give a yellow oil. Within a few days, small yellow crystals had begun to form. On prolonged standing, the number of crystals increased while the amount of oily material decreased. Some of the crystals were removed in an inert atmosphere, blotted dry, and analysed. Anal. Found (av.): C, 9.8; H, 1.9. *Sb<sub>2</sub>Et<sub>4</sub>*:*CdI<sub>2</sub>* calcd.: C, 13.2; H, 2.7; *Sb<sub>2</sub>Et<sub>4</sub>*:*2CdI<sub>2</sub>* calcd.: C, 8.8; H, 1.9%. (mp 160°C dec.). EDX analysis showed that the crystals contained Sb, Cd and I. A crystal suitable for X-ray diffraction studies was found and mounted under a nitrogen atmosphere in a capillary tube.

### 2.9. Crystallography, *Et<sub>4</sub>Sb<sub>2</sub> · 2CdI<sub>2</sub>*

A representative light yellow tabular crystal was used for data collection. Intensity measurements were made on a Nicolet R3m/V diffractometer using graphite monochromated Mo *K<sub>α</sub>* radiation at 20°C. Cell parameters were derived by least-squares calculations from angular settings of 30 reflections measured between 19° < 2θ < 40°. Other crystal data are summarised in Table 1. Three standard reflections monitored every 197 reflections showed an 8% decrease in intensity over the data collection period.

TABLE 1. Summary of crystal structure data for the adduct *Et<sub>4</sub>Sb<sub>2</sub> · 2CdI<sub>2</sub>*

(a) Crystal data	
Formula	Cd <sub>2</sub> I <sub>4</sub> Sb <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub>
Mol wt	1092.2
Crystal size	0.50 × 0.44 × 0.26 mm
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	8.179(2)
<i>b</i> (Å)	8.913(2)
<i>c</i> (Å)	16.220(2)
α (deg)	77.80(2)
β (deg)	85.13(2)
γ (deg)	79.23(2)
<i>V</i> (Å <sup>3</sup> )	1134.1(5)
<i>Z</i>	2
<i>D</i> (calc.) (g cm <sup>-3</sup> )	3.20
<i>F</i> (000)	956
Mo <i>K<sub>α</sub></i> radiation, λ (Å)	0.71073
μ (Mo <i>K<sub>α</sub></i> ) (cm <sup>-1</sup> )	95.96
(b) Data collection	
Temperature (°C)	20
2θ limits (deg)	3.5–65
ω-scan range (deg)	1.5
Scan rate (deg min <sup>-1</sup> )	5.00–29.30
Total no. of data (± <i>h</i> , ± <i>k</i> , ± <i>l</i> )	8270
No. of data <i>F</i> > 6σ <i>F</i>	3679
Abs cor	0.143(max), 0.033(min)
Final <i>R</i> and <i>R<sub>w</sub></i>	0.074 and 0.089
Weight <i>w</i>	[σ( <i>F<sub>o</sub></i> ) + 0.000541 <i>F<sub>o</sub></i> <sup>2</sup> ] <sup>-1</sup>

Intensity data were corrected for decomposition and Lorentz and polarisation effects. A numerical absorption correction was applied [43], the maximum and minimum transmission factors being 0.143 and 0.033 respectively. The atomic scattering factors for neutral atoms were taken from reference [44] and were corrected for anomalous dispersion using values from the same reference. The program used for the least-squares refinement was that due to Sheldrick [43].

The structure was solved by direct methods and refinement effected by full matrix least-squares methods. Anisotropic thermal parameters were introduced for all non-hydrogen atoms (Table 2). Hydrogen atoms were located in geometrically idealised positions (C–H = 0.96 Å) with a single fixed isotropic thermal parameter.

## 3. Results

### 3.1. Synthesis and vapour pressures of *Et<sub>4</sub>Sb<sub>2</sub>* and *Me<sub>4</sub>Sb<sub>2</sub>*

*Et<sub>4</sub>Sb<sub>2</sub>* was first reported in 1935 from the reaction of ethyl radicals with antimony [45]. It has also been made by thermal decomposition of *Et<sub>2</sub>SbH* [46], reduction of *Et<sub>3</sub>Sb* by sodium in liquid ammonia followed by

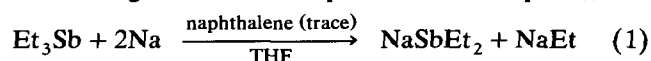
TABLE 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $\text{\AA}^2 \times 10^3$ ) for  $\text{Et}_4\text{Sb}_2 \cdot 2\text{CdI}_2$ 

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a$
Sb(1)	3313(2)	6978(1)	1668(1)	43.0(4)
Sb(2)	2812(2)	7770(1)	3253(1)	51.7(5)
Cd(1)	2415(2)	9298(2)	226(1)	60.4(5)
Cd(2)	2288(2)	5565(2)	4734(1)	66.7(6)
I(1)	305(2)	12094(1)	298(1)	59.2(5)
I(2)	4735(2)	9104(2)	-1082(1)	56.0(5)
I(3)	1159(2)	2811(2)	4795(1)	61.3(5)
I(4)	3948(2)	6140(2)	5998(1)	59.4(5)
C(1)	2271(32)	4841(30)	1901(18)	92(12)
C(2)	459(35)	5048(36)	2206(18)	110(16)
C(3)	5969(26)	6108(30)	1586(14)	75(10)
C(4)	6490(32)	5161(35)	952(23)	130(19)
C(5)	5173(31)	8531(25)	3400(13)	69(9)
C(6)	4763(57)	9999(39)	3773(22)	161(25)
C(7)	1125(33)	9831(29)	2990(16)	90(11)
C(8)	-479(29)	9724(37)	2711(21)	128(16)

<sup>a</sup> Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalised  $U_{ij}$  tensor.

oxidation of the  $\text{NaSbEt}_2$  with 1,2 dichloroethane [47], treatment of the product of reaction of sodium and antimony in liquid ammonia with bromoethane [48], and reduction of  $\text{Et}_2\text{SbBr}$  with magnesium in THF [49]. We have prepared  $\text{Et}_4\text{Sb}_2$  in good yield by the last method. The same method was used to prepare  $\text{Me}_4\text{Sb}_2$ .

Because this is a rather time consuming preparation, involving syntheses of the three intermediates  $\text{R}_3\text{Sb}$ ,  $\text{R}_3\text{SbBr}_2$  and  $\text{R}_2\text{SbBr}$ , we have also attempted to find a new, convenient route to the distibines. We found that sodium reduction of  $\text{Et}_3\text{Sb}$  will proceed in THF in the presence of a catalytic amount of naphthalene, eliminating the need for liquid ammonia (eqn. (1)).



Oxidation of the salt with dichloroethane can then be achieved in an appropriate organic solvent. However, the yield was low and it was difficult to remove the traces of naphthalene. This method was not pursued further. The other published methods seemed less attractive than our chosen method.

Purification of the  $\text{Et}_4\text{Sb}_2$  was achieved by distillation at  $75^\circ\text{C}$  under vacuum and with protection from light. Earlier reports [46] indicate that it decomposes at temperatures as low as  $50^\circ\text{C}$  on attempted distillation. This may be due to light sensitivity rather than thermal instability. We have observed that  $\text{Et}_4\text{Sb}_2$  deposits antimony metal and forms  $\text{Et}_3\text{Sb}$  when exposed to light. Similar observations apply to diethylcadmium which deposits cadmium in minutes at  $30^\circ\text{C}$  in daylight [50]. Although one group suggested that the original material isolated by Paneth and Loleit [45] was actually

an oxide, no elaboration was offered [48]. We have observed the parent and fragment peaks for  $\text{Et}_2\text{SbO-SbEt}_2$  in the mass spectrum of the distibine which was partially oxidized by deliberate exposure to traces of oxygen before admission to the mass spectrometer sample port.

The mass spectrum of  $\text{Et}_4\text{Sb}_2$  agreed with that previously reported [51], revealing elimination of both ethyl radicals and ethene. There is no evidence of fragments arising from cleavage of the carbon-carbon bonds of the ethyl groups, indicating that the new antimony source will not be a serious source of carbon contamination of epilayers, particularly at low growth temperatures. The mass spectrum also exhibits peaks assigned to  $\text{Et}_3\text{Sb}$ ,  $\text{Sb}_4$ ,  $\text{Et}_2\text{Sb}_3$ , and  $\text{Et}_4\text{Sb}_3$  which might arise from decomposition during sample heating.

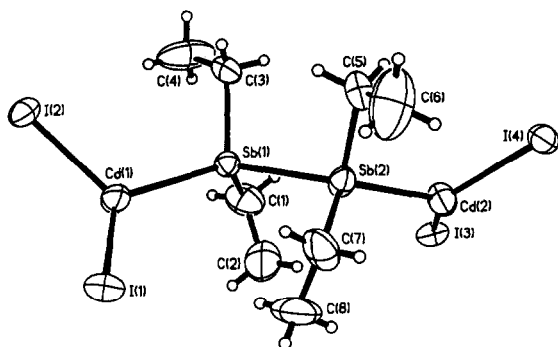
Vacuum distillation was also used to purify  $\text{Me}_4\text{Sb}_2$ . The mass spectrum of this compound does not indicate formation of antimony carbide fragments, and hence carbon contamination may not be a problem with this source.

The vapour pressure of  $\text{Et}_4\text{Sb}_2$  measured at  $18^\circ\text{C}$  was found to be 0.006 mm Hg, which is in agreement with extrapolation of literature distillation data [45,47-49]. We have found that  $\text{Me}_4\text{Sb}_2$  is forty times more volatile, with a vapour pressure of 0.24 mm Hg at  $18^\circ\text{C}$ .

### 3.2. Attempted adduct purification of $\text{Et}_4\text{Sb}_2$ and crystal structure of the $\text{CdI}_2$ adduct

The purification of MOCVD alkyl feedstocks by reversible adduct formation has been patented [52]. Alkyl tellurides and ditellurides form adducts with salts of copper, silver, mercury, and cadmium [53,54]. We were therefore interested to attempt purification of distibines in this manner. Treatment of  $\text{Et}_4\text{Sb}_2$  with  $\text{CdI}_2$  in THF followed by removal of solvent yielded a stable, crystalline polymeric adduct of composition  $[\text{Et}_4\text{Sb}_2 \cdot 2\text{CdI}_2]_n$ . The crystal structure has been determined and is shown in Figs. 1 and 2. Important bond distances and angles are presented in Table 3. There are a number of interesting features of the structure.

The structure consists of chains of iodide-bridged  $\text{Et}_4\text{Sb}_2 \cdot 2\text{CdI}_2$  units which have  $\text{CdI}_2$  bridged to each antimony atom. As shown in Fig. 2, the cadmium, antimony and two iodine atoms form a trigonal planar arrangement around cadmium, and two weak axial bonds to the iodides of adjacent units gives distorted trigonal bipyramidal coordination to cadmium. The Sb-Sb distance of 2.784(2) Å is shorter than is found in the metal (2.90 Å), or in the more closely related molecules  $\text{Me}_4\text{Sb}_2$  (2.86 Å) [55] and  $(\text{C}_5\text{Me}_5)_4\text{Sb}_4$  (2.856(1) Å) [56]. The ethyl(C)-Sb-Sb bond angle of  $102^\circ$  (av.) is somewhat larger than that found in  $\text{SbX}_3$  compounds where  $\text{X} = \text{C}_5\text{H}_5$  [57],  $p\text{-ClC}_6\text{H}_4$  [58] or a

Fig. 1. Molecular structure of the adduct  $Et_4Sb_2 \cdot 2CdI_2$ .

halide [59]. The Cd–Sb–C angles average  $120^\circ$ . The  $SbEt_2$  groups are skewed with respect to each other. This orientation could correspond to a minimum on the rotation potential energy curve about the Sb–Sb bond which is expected to have some multiple bond character [60].

### 3.3. Reactions of $Et_4Sb_2$ with $Te$ , $Et_2Te$ and $Me_2Cd$

The ease with which the distibine formed an adduct with  $CdI_2$  prompted an investigation of its reactivity with species that could be encountered in the gas mixing channel or reactor cell of the MOCVD reactor. A 1:1 adduct was formed on reaction of  $Et_4Sb_2$  with neat  $Me_2Cd$  in the liquid phase. The insoluble compound is most likely polymeric, with a backbone of  $[-Cd-Sb-Sb-]_n$  chains. It would be of interest to determine the crystal structure of this species, and attempts are underway to grow crystals from vapour phase mixing of the reactants. Reaction does occur slowly between the vapours at room temperature. Significant reaction between the vapours seems less likely

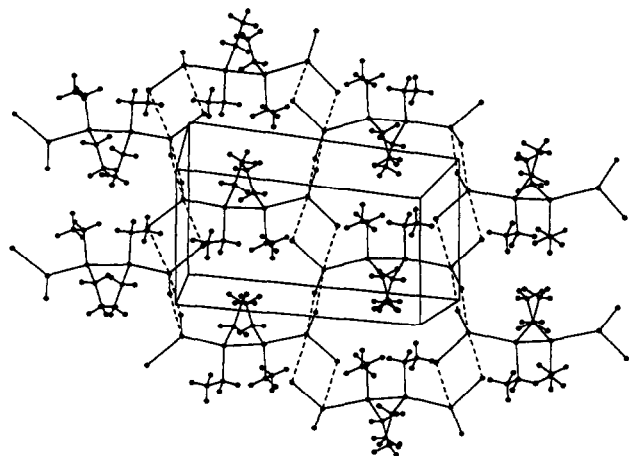


Fig. 2. Packing diagram showing the interaction between chains.

TABLE 3. Bond lengths and angles for  $Et_4Sb_2 \cdot 2CdI_2$ 

(a) Bond lengths ( $\text{\AA}$ )			
Sb(1)–Sb(2)	2.784(2)	Sb(1)–Cd(1)	2.822(2)
Sb(1)–C(1)	2.179(28)	Sb(1)–C(3)	2.169(20)
Sb(2)–Cd(2)	2.821(2)	Sb(2)–C(5)	2.210(27)
Sb(2)–C(7)	2.069(23)	Cd(1)–I(1)	2.772(2)
Cd(1)–I(2)	2.736(2)	Cd(2)–I(3)	2.760(2)
Cd(2)–I(4)	2.735(3)	C(1)–C(2)	1.513(38)
C(3)–C(4)	1.452(45)	C(5)–C(6)	1.526(43)
C(7)–C(8)	1.450(40)		
Cd(1) $\cdots$ I(1A)	3.002(2)	Cd(1) $\cdots$ I(2B)	3.466(2)
Cd(2) $\cdots$ I(3C)	3.034(2)	Cd(2) $\cdots$ I(4D)	3.404(2)

Second atom generated by transform:

A:  $-x, 2.0 - y, -z$   
 B:  $1.0 - x, 2.0 - y, -z$   
 C:  $-x, 1.0 - y, 1.0 - z$   
 D:  $1.0 - x, 1.0 - y, 1.0 - z$

(b) Bond angles (deg)			
Sb(2)–Sb(1)–Cd(1)	119.0(1)	Sb(2)–Sb(1)–C(1)	101.1(8)
Cd(1)–Sb(1)–C(1)	119.3(7)	Sb(2)–Sb(1)–C(3)	103.4(7)
Cd(1)–Sb(1)–C(3)	109.5(6)	C(1)–Sb(1)–C(3)	102.3(9)
Sb(1)–Sb(2)–Cd(2)	122.1(1)	Sb(1)–Sb(2)–C(5)	102.4(6)
Cd(2)–Sb(2)–C(5)	106.0(5)	Sb(1)–Sb(2)–C(7)	100.9(8)
Cd(2)–Sb(2)–C(7)	119.1(7)	C(5)–Sb(2)–C(7)	103.9(10)
Sb(1)–Cd(1)–I(1)	123.3(1)	Sb(1)–Cd(1)–I(2)	111.9(1)
I(1)–Cd(1)–I(2)	120.1(1)	Sb(1)–Cd(1)–I(1A)	97.5(1)
I(1)–Cd(1)–I(1A)	92.5(1)	I(2)–Cd(1)–I(1A)	102.1(1)
Sb(2)–Cd(2)–I(3)	125.4(1)	Sb(2)–Cd(2)–I(4)	108.2(1)
I(3)–Cd(2)–I(4)	124.0(1)	Sb(2)–Cd(2)–I(3A)	96.3(1)
I(3)–Cd(2)–I(3A)	91.9(1)	I(4)–Cd(2)–I(3A)	97.7(1)
Sb(2)–Cd(2)–I(4A)	79.2(1)	I(3)–Cd(2)–I(4A)	88.0(1)
I(4)–Cd(2)–I(4A)	87.0(1)	I(3A)–Cd(2)–I(4A)	174.3(1)
Cd(1)–I(1)–Cd(1A)	87.5(1)	Cd(2)–I(3)–Cd(2A)	88.1(1)
Cd(2)–I(4)–Cd(2B)	93.0(1)	Sb(1)–C(1)–C(2)	113.8(19)
Sb(1)–C(3)–C(4)	114.6(18)	Sb(2)–C(5)–C(6)	108.3(22)
Sb(2)–C(7)–C(8)	116.4(20)		

at elevated temperatures, and we do not expect pre-reaction to be a major problem under growth conditions.

A slow reaction occurs when liquid samples of  $Et_4Sb_2$  and  $Et_2Te$  are mixed. Substantial amounts of starting material were still present after 1 month. The major products are  $Et_3Sb$ , the known compound  $Et_2SbTeSbEt_2$  [42], and  $Et_2SbTeEt$ , which has not previously been reported. It is known [61] that  $R_2SbTeR'$  compounds rearrange to  $R_3Sb$  and  $RSb(TeR')_2$ , and a reaction of this type is possibly the source of  $Et_3Sb$ . However, we have not detected the presence of  $EtSb(TeEt)_2$ . It is also possible that  $Et_3Sb$  results from an interaction between  $Et_2SbTeEt$  and  $Et_2SbSbEt_2$ , and  $Et_2SbTeSbEt_2$  would be a co-product of such a reaction. These ideas need to be tested further.

We have found that  $Et_2SbTeEt$  is formed as the only major product when the distibine is treated with

the ditelluride EtTeTeEt. We have also observed that Et<sub>2</sub>SbTeSbEt<sub>2</sub> is formed in the direct reaction between Et<sub>2</sub>SbSbEt<sub>2</sub> and tellurium metal. Some of these mixed Sb–Te compounds may be interesting single source compounds for MOCVD applications, and we intend to explore this chemistry further.

Although Te readily inserts into Et<sub>2</sub>SbSbEt<sub>2</sub>, no reaction occurs when the distibine is stirred with Hg or Cd metals at room temperature.

#### 3.4. Thermal decomposition of Me<sub>4</sub>Sb<sub>2</sub>

Pyrolysis of tetramethyldistibine in hydrogen at the relatively low temperature of 300°C does yield a film of antimony. Analysis by XPS reveals no detectable impurities. The kinetics and products of this thermal decomposition reaction certainly warrant further investigation, and MOCVD growth studies are currently under way.

#### 3.5. MOCVD growth of p-type Sb doped MCT

We have examined the application of tetraethyldistibine in the p-doping of MCT by low temperature MOCVD. MCT films were grown in an MR Semicon Quantax 226 MOCVD horizontal reactor using dimethylcadmium, diethyltellurium and elemental mercury with hydrogen carrier gas at atmospheric pressure. The substrates were semi-insulating GaAs (100) 2° misoriented towards (110) which were degreased and etched in 5:1:1 H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O. Initially, a buffer layer of CdTe (*ca.* 1.5 μm in thickness) was deposited prior to the MCT in order to prevent the indiffusion of Ga from the substrate. Subsequently, growth was conducted by an interdiffused multilayer process (IMP) [62] using a period of 100 nm with the Sb doping introduced during the CdTe portion of the growth cycle. The growth rate at 280°C was *ca.* 1 μm/h. The layers were subsequently interdiffused in the reactor under Hg vapour at a temperature of 340°C. The presence of antimony in the epilayers was confirmed by qualitative SIMS analysis and inductively coupled atomic emission spectrometry (ICPAES) of material collected on glass slides placed adjacent to the GaAs substrates. Assessment of the composition and thickness of the MCT films was made from IR transmission spectra. Hall effect and resistivity measurements were performed on cloverleaf-patterned samples [63] using a magnetic field strength of 1.9 kG at temperatures of 77 K and 300 K.

The antimony-doped layers of composition Hg<sub>1-x</sub>-Cd<sub>x</sub>Te with *x* = 0.60 showed uniformity of conduction type across the wafer as evidenced by a positive Hall coefficient of 1 × 10<sup>3</sup> cm<sup>3</sup> C<sup>-1</sup>. The mobility of the doped layers was in the range from μ = 58–65 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> with carrier concentrations from 8 × 10<sup>15</sup> to

1 × 10<sup>16</sup> cm<sup>-3</sup> and resistivity of *ca.* 11 Ω cm at 77 K. In comparison, equivalent layers of MCT (Hg<sub>1-x</sub>Cd<sub>x</sub>Te with *x* = 0.60) grown without the Sb doping were n-type with μ ≈ 1 × 10<sup>2</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and n<sub>e</sub> ≈ 2.5 × 10<sup>15</sup> cm<sup>-3</sup> at 77 K. The Hall coefficient for the undoped layers was negative and of magnitude 1.0 × 10<sup>3</sup> cm<sup>3</sup> C<sup>-1</sup>. The presence of the high positive values of Hall coefficient at both room temperature and 77 K in the wafers doped with tetraethyldistibine indicates an extrinsic p-doping of the MCT. The Hall devices were used as simple photoconductive detectors, and demonstrated sensitivity to 1.3 μm laser radiation. Further details, including formation of n/p diodes will be reported elsewhere.

#### 3.6. Low temperature MOCVD growth of InSb with Et<sub>4</sub>Sb<sub>2</sub>

The tetraethyldistibine was also used to grow epitaxial InSb by MOCVD. Growth was achieved on lattice matched MCT/GaAs substrates at temperatures as low as 330°C using 1:1 doses of trimethylindium and tetraethyldistibine and hydrogen carrier gas. Reasonable growth rates (*ca.* 2–3 μm/h) were achieved. The layers were examined by TEM and EDX. The growth is limited by the cracking efficiency of Me<sub>3</sub>In, approaching 100% at 390°C. Further details will be published in a forthcoming paper [64]. The low growth temperature should allow InSb/MCT heterojunctions and superlattices to be grown with minimal reaction at the hetero-interface.

## 4. Conclusions

Tetraethyldistibine is a useful low vapour pressure antimony feedstock for the low temperature doping of metal alloys. We have demonstrated low temperature p-doping of as-grown MCT. Further experiments are planned to quantify the incorporation and activation of antimony in HgTe and other related II–VI (12–16) epilayers. The compound has also been used for low temperature growth of InSb, but related compounds of higher volatility may prove more useful for this purpose. Work is continuing on optimising the synthetic route to tetraethyldistibine and related compounds. Methods of purifying low volatility compounds will be developed further in order to scale up their production. Aspects of this work are covered by a provisional patent application [65]. Subsequent to this work, a patent covering the use of Et<sub>4</sub>As<sub>2</sub> was published [66].

## Acknowledgments

We thank A. Coleman for synthesis and purification of dimethyl cadmium, G. Brinson for fabrication of the

Hall devices, M. Crarey for FTIR measurements, M.H. Kibel for substrate preparation, EDX and XPS spectra, S. Duck for mass spectra, R. Pierson for ICPAES and C. Frost for SIMS analysis. The permission of the Executive General Manager, Reseach, Telecom Australia, to publish this work is acknowledged. Partial support was provided under the Generic Technology component of the Industry Research and Development Act 1986, Grant Nos. 15019 and 15052. We thank the Australian Government and The Broken Hill Proprietary Company Limited for an Australian Postgraduate Industry Research Award (to K.D.H.).

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