Compositionally Tunable Ternary $\text{Bi}_2(\text{Se}_{1-x}\text{Te}_x)_3$ and $(\text{Bi}_{1-y}\text{Sb}_y)_2\text{Te}_3$ Thin Films via Low Pressure Chemical Vapour Deposition

Sophie L. Benjamin\textsuperscript{a,b}, C. H. (Kees) de Groot\textsuperscript{c}, Chitra Gurung\textsuperscript{a,d}, Samantha L. Hawken\textsuperscript{a}, Andrew L. Hector\textsuperscript{a}, Ruomeng Huang\textsuperscript{e}, Marek Jura\textsuperscript{a}, William Levason\textsuperscript{a}, Eleanor Reid\textsuperscript{a}, Gillian Reid\textsuperscript{a}, Stephen P. Richards\textsuperscript{a} and Gavin B. G. Stenning\textsuperscript{a}

The inherently rapid ligand substitution kinetics associated with the novel and chemically compatible precursors, $[\text{MCl}_3(\text{EnBu}_2)_3]$ (M = Sb, Bi; E = Se, Te), enable CVD growth of ternary $\text{Bi}_2(\text{Se}_{1-x}\text{Te}_x)_3$ and $(\text{Bi}_{1-y}\text{Sb}_y)_2\text{Te}_3$ thin films with very good compositional, structural and morphological control, for the first time. X-ray diffraction data follow Vegard’s law and Raman bands shift linearly with the atom substitutions, indicating very well-distributed solid solutions.

Antimony and bismuth selenide and telluride, $\text{M}_2\text{E}_3$ (M = Sb, Bi; E = Se, Te), are layered narrow bandgap semiconductors; $\text{Bi}_2\text{Se}_3$ 0.24 eV, $\text{Bi}_2\text{Te}_3$ 0.16 eV and $\text{Sb}_2\text{Te}_3$ 0.28 eV.\textsuperscript{1–2} Their highly anisotropic dielectric constant ($\varepsilon < 10^2$ within a 2 KHz to 2 MHz range)\textsuperscript{18} are required for high electrical conductivities, whilst being thermally insulating. Electrical conductivities ($\sigma$) reported for the layered hexagonal $\text{M}_2\text{E}_3$ materials produced via a range of deposition methods are around 550 S cm\textsuperscript{-1} ($\text{Bi}_2\text{Se}_3$), 340–1780 S cm\textsuperscript{-1} ($\text{Bi}_2\text{Te}_3$)\textsuperscript{b,d} and 104–1695 S cm\textsuperscript{-1} ($\text{Sb}_2\text{Te}_3$).\textsuperscript{9,13–15} $\text{Sb}_2\text{Se}_3$, on the other hand, adopts an orthorhombic structure and with its comparatively larger band gap (1.1 eV), has intrinsically low electrical conductivity ($10^{-6}–10^{-7}$ S cm\textsuperscript{-1}),\textsuperscript{16} however, its high absorption coefficient (> 10\textsuperscript{5} cm\textsuperscript{-1})\textsuperscript{17} and dielectric constant (29–18 within a 2 KHz to 2 MHz range)\textsuperscript{18} are attractive for photovoltaics.\textsuperscript{19,20} These materials are also important topological insulators\textsuperscript{21,22} and candidates for spintronic devices.\textsuperscript{14}

As a scalable and relatively inexpensive processing method, chemical vapour deposition (CVD) is very widely used for thin film deposition.\textsuperscript{23} A number of CVD approaches have been employed for binary $\text{M}_2\text{E}_3$ film growth, most of which use multiple precursor sources, e.g. $\text{Bi}_2\text{Se}_3$: $\text{BiMe}_3 + \text{SeEt}_2 / \text{H}_2$;\textsuperscript{7} $\text{Bi}_2\text{Te}_3$: $\text{BiMe}_3 + \text{TePiPr}_2$;\textsuperscript{8} $\text{Sb}_2\text{Te}_3$: $\text{SbR}_3 (\text{R} = \text{Me, Et}) + \text{TePiPr}_2$ (R = Et, iPr).\textsuperscript{24,25} However, single source precursors (containing the metal and chalcogen within a single molecule) can offer advantages, including good control of the stoichiometry, more efficient precursor use, and easier-to-handle precursors (less hydrolytically sensitive and less pyrophoric). A small number of single source precursors for CVD of binary $\text{M}_2\text{E}_3$ materials have been reported, including $[\text{Bi}(\text{SePr}_2)_3\text{N}]_3$ (R = Ph, iPr),\textsuperscript{16,27} whilst $[\text{Sb}(\text{TePiPr}_2)_3\text{N}]_3$ \textsuperscript{38} and $[\text{SbSeC}_5\text{H}_3(\text{Me-3})\text{N}]_3$ \textsuperscript{29} have been used to deposit $\text{Sb}_2\text{Te}_3$ and $\text{Sb}_2\text{Se}_3$, respectively, via aerosol assisted (AA)CVD. $[\text{MeSb}(\text{E}n\text{Bu}_2)_2\text{N}]_3$ (E = Se, Te) produce $\text{Sb}_2\text{Se}_3$ and $\text{Sb}_2\text{Te}_3$ thin films via low pressure (LP)CVD.\textsuperscript{15,30} We have used molecular complexes of early transition metal and main group chlorides, bearing neutral chalcogenoether ligands for LPCVD of binary metal chalcogenide thin films.\textsuperscript{31–34} The possibility of selective deposition of oriented films onto defined regions of lithographically patterned substrates has also been realised using these types of precursors.\textsuperscript{12} This selectivity could bring significant advantages in device fabrication, since, if the chalcogenide material can be deposited only onto pre-defined regions of patterned substrates, this would reduce the number of processing steps required (e.g. removing the need for back-etching), as well as reducing the volume of the chalcogenide material required.

Whilst commercial thermoelectric devices based upon n-type $\text{Bi}_2\text{Te}_3$ and p-type $\text{Sb}_2\text{Te}_3$ are available, significantly enhanced thermoelectric properties have been reported for ternary phases and superlattices of $\text{Bi}_2\text{Te}_3$ and $\text{Bi}_2\text{Te}_3$.\textsuperscript{35,36} The ability to control the composition, morphology and crystallite sizes in thin films of the related ternary materials is therefore of considerable interest to allow optimisation of their properties for various applications, most notably thermoelectrics and topological insulators.\textsuperscript{37–41} For n-type $\text{Bi}_2\text{Te}_3$, this is best achieved by introducing Se, forming a solid solution of $\text{Bi}_2(\text{Se}_{1-x}\text{Te}_x)_3$. Optimisation of p-type $\text{Sb}_2\text{Te}_3$ can be
achieved by incorporation of Bi, in (Bi₂Sb₂)Te₃. Previous work has
mainly involved solid state or solution processing methods to
produce the ternary materials, and usually as bulk materials rather
than thin films.35-41 CVD of thin films of these key ternary thin film
materials with good compositional control, as well as structural/morphological control, would open up exciting application
prospects. However, this is particularly challenging by conventional
CVD methods involving multiple precursors.

We report here the new molecular precursors, [BiCl₃(SeⁿBu₂)₃],
[SbCl₃(SeⁿBu₂)₃] and [SbCl₃(TeⁿBu₂)₃], demonstrate their utility
as single source CVD precursors for binary Bi₂Se₃, Sb₂Se₃ and
Sb₂Te₃ films, respectively, and, most significantly, we show that
LPCVD using the appropriate combination of (chemically
similar) precursors from this series, produces thin films of the
two key ternary solid solutions, Bi₂(Se₁−ₓTex)₃ and (Bi₁−ySby)₂Te₃
with very good compositional, structural and morphological
control.

Precursors: Whilst a number of CVD reagents for Bi₂Se₃ thin film
deposition are known (vide supra), the previously unknown
analogues of the precursor we used to deposit Bi₂Te₃, i.e.
[BiCl₃(SeⁿBu₂)₃], were prepared with the intention of achieving
chemical compatibility between the precursor types. The target
compounds, [BiCl₃(SeⁿBu₂)₃], [SbCl₃(SeⁿBu₂)₃] and [SbCl₃(TeⁿBu₂)₃],
were obtained in good yield as illustrated in Scheme 1, and have
been shown to be suitable for LPCVD of the respective binary M₂E₃
thin films, with compositional, structural and electrical properties
indicative of high quality materials (ESI).

Scheme 1: Synthesis of the precursor complexes

We have shown previously that n-type Bi₂Te₃ can be selectively
deposited into the TiN wells of lithographically patterned TiN/SiO₂
substrates using the precursor [BiCl₃(SeⁿBu₂)₃] 12 therefore, it was
important to establish whether this could also be achieved for the p-
type Sb₂Te₃. SEM images from depositions using ~15 mg of
[SbCl₃(TeⁿBu₂)₃] at 723 K revealed that this is indeed the case (Fig.
1a). Quantitative EDX analysis revealed an Sb : Te ratio of 41 : 59
% and grazing incidence XRD data are consistent with R-3mH Sb₂Te₃
(Fig. 1b).

Figure 1: (a) SEM image with EDX mapping and (b) grazing incidence XRD
pattern from Sb₂Te₃ selectively deposited from [SbCl₃(SeⁿBu₂)₃] into 30
µm TiN holes and an indexed bulk pattern of Sb₂Te₃.42 The TiN substrate
peaks are marked by *.

**LPCVD of ternary Bi₂(Se₁−ₓTex)₃ thin films:**

Our approach to deposit thin films of the ternary chalcogenide,
Bi₂(Se₁−ₓTex)₃, exploits the inherent high lability of Bi(III) complexes
with neutral donor ligands in solution. We have utilised the rapid
ligand substitution kinetics of [BiCl₃(EⁿBu₂)₃] (E = Se, Te) to create
two ternary/thio-seleno complexes, Bi₂Se₃ by combining
various ratios of the precursors in CH₂Cl₂ solution prior to the CVD
experiments. The relatively similar temperatures required for LPCVD
of each of the binary M₂E₃ phases from this homologous pair of
precursors was also promising for the LPCVD of the required Bi₂(Se₁−
ₓTex)₃ ternary phase. At first sight, the need for a higher temperature
for the Bi₂Se₃ deposition (550 °C from [BiCl₃(SeⁿBu₂)₃]) in comparison
to that for LPCVD growth of Bi₂Te₃ (450 °C) was unexpected.
However, this most likely reflects the presence of the weaker Te––C
bonds in the latter (cf. the Se–C bonds in [BiCl₃(SeⁿBu₂)₃]), arising
from the orbital energy mismatch of the C and Te atoms. Hence,
while the volatility of the higher MWT [BiCl₃(SeⁿBu₂)₃] precursor is
expected to be lower than for the [BiCl₃(SeⁿBu₂)₃] precursor, this is
offset by its lower thermal stability.

To test the hypothesis that these two precursors would be
compatible for the optimisation of the target ternary Bi₂(Se₁−ₓTex)₃
phase by LPCVD, we initially studied the solution behaviour of
[BiCl₃(SeⁿBu₂)₃] and [BiCl₃(TeⁿBu₂)₃], and mixtures thereof, by
¹⁷⁷Se(H) and ¹²⁵Te(H) NMR spectroscopy in CH₂Cl₂ solution (Fig. S7).
Each of solutions (i) to (iv) gave only one singlet at room
temperature, indicating a single species in solution. Introducing
increasing amounts of [BiCl₃(SeⁿBu₂)₃] to a solution of [BiCl₃(TeⁿBu₂)₃]
leads to a progressive shift of δ(¹⁷⁷Se) to lower frequency, while
δ(¹²⁵Te) moves to higher frequency (cf. the individual parent complexes).
Lowering the temperature to ~80 °C causes only slight
broadening of the resonances for each of the parent complexes (i)
and (iv), and this was replicated for the mixed Se/Te samples (iii) and
(iii)). This behaviour is consistent with rapid ligand exchange
(scrambling) in CH₂Cl₂ solution and the high lability of the BiCl₃
acceptor fragment, suggesting that the species present in solution are
of the form [BiCl₃(SeⁿBu₂)₃−1m(SeⁿBu₂)₃] (m = 0 to 1) and hence
this may be a possible reagent for LPCVD of the target ternary Bi₂(Se₁−
ₓTex)₃ phase.

To test this hypothesis, a series of LPCVD experiments were
undertaken by mixing different ratios of the two precursors to
produce [BiCl₃((SeⁿBu₂)₃−1m(SeⁿBu₂)₃)] with different values of a (from
0 to 3). Depositions were performed at 550 °C/0.05 mmHg onto SiO₂-
coated silicon substrates. In each case, reflective silvery films were
obtained. EDX analyses (Fig. 2) revealed that the %Te content
increases with increasing Te precursor amount, with a concomitant
decrease in the %Se present. These data indicate very good control
of the composition of the Bi₂(SeₓTe₁−ₓ)₃ ternary material using the
[BiCl₃(SeⁿBu₂)₃]/[BiCl₃(SeⁿBu₂)₃] precursor system. The %Te does not
increase linearly with the fraction of the Te precursor used. Instead,
we shows an enhancement in Te deposition. The enhancement factor
can be calculated by the Te precursor fraction using Equation 1,

\[ \%Te = 0.6 \times \frac{m}{1 + (a-1)m} \]  

(Equation 1)
where \( m \) is the Te precursor fraction and \( \alpha \) is defined as the proposed ‘enhancement factor’. The dotted lines in Fig. 2b represent the calculated %Te values using an enhancement factor, \( \alpha \), of 2.5 and correspond well with the experimental values. This enhanced deposition of Te can be accounted for at least in part by the lower thermal stability of the \([\text{BiCl}_3(\text{Te}^\text{Bu}_2)_3]\) precursor due to the weaker Te–C bonds.

Figure 2 (a) EDX spectra and (b) relationship between film composition and fraction of \([\text{BiCl}_3(\text{Te}^\text{Bu}_2)_3]\) used in the deposition of ternary Bi\(_2\)(Se\(_{1-x}\)Tex)\(_3\) films.

SEM (Figure 3) analysis shows that the ternary films, like the binary parent materials, are polycrystalline, with good coverage across the substrate. In each case, film thicknesses of ca. 1 \( \mu \)m were obtained. The hexagonal crystallites are clearly visible, although their orientation varies; for the \( \text{Bi}_2\text{Se}_3 \) films, the crystallites appear to be aligned perpendicular to the substrate, whereas in the ternary and \( \text{Bi}_2\text{Te}_3 \) films most of the crystallites tend to lie parallel to the surface.

Figure 3 SEM images showing the morphologies of the \( \text{Bi}_2\text{Se}_3 \) (a), \( \text{Bi}_2\text{Te}_3 \) (e) and ternary \( \text{Bi}_2(\text{Se}_{1-x}\text{Te}_x)_3 \) (b)-(d) films deposited by LPCVD under similar conditions (550 °C/0.05 mmHg) onto SiO\(_2\)-coated silicon substrates.

The phase purity and crystallinity of the as-deposited films were examined by grazing incidence XRD analysis (Fig. 4a). All five films are isostructural, with no other phases detectable. A systematic shift of all the characteristic diffraction peaks with increasing Te composition is evident. Broadening of the 015 peak (Fig. 4b) for the \( \text{Bi}_2(\text{Se}_{0.8}\text{Te}_{0.2})_3 \), \( \text{Bi}_2(\text{Se}_{0.5}\text{Te}_{0.5})_3 \), \( \text{Bi}_2(\text{Se}_{0.3}\text{Te}_{0.7})_3 \) films can be observed, consistent with increased disorder in the structures due to Te doping. This disorder is also consistent with the decrease of the crystallite sizes for these three ternary compositions seen in Fig. 3. The lattice parameters (\( \alpha \), \( c \)) of all five compositions were refined against the \( \text{Bi}_2\text{Se}_3 \) phase from the ICSD.\(^{43}\) Linear increases of both \( \alpha \) and \( c \) with increasing Te content are observed (Fig. 4c), consistent with Vegard’s law, i.e. well distributed solid solutions of the ternary \( \text{Bi}_2(\text{Se}_{1-x}\text{Te}_x)_3 \).

The vibrational properties of the as-deposited \( \text{Bi}_2(\text{Se}_{1-x}\text{Te}_x)_3 \) films were also studied by Raman spectroscopy. The spectra are shown in Fig. 5, where peaks are fitted using the Gaussian equation. For \( \text{Bi}_2\text{Te}_3 \) (Fig. 5a), two peaks positioned at 129 and 171 cm\(^{-1}\) can be assigned as \( E_g^2 \) (in-plane) and \( A_{1g}^2 \) (out-of-plane) modes, respectively, similar to previous reports.\(^{44}\) These two vibrational modes are also present in the other four films, although they shift progressively to lower wavenumbers with increasing Te content (Fig. 5f). These results provide strong evidence for a very well-distributed solid solution.\(^{38,39}\) An additional peak at ca. 120 cm\(^{-1}\) is detected for \( \text{Bi}_2(\text{Se}_{0.7}\text{Te}_{0.3})_3 \) and \( \text{Bi}_2\text{Te}_3 \) (Fig. 5d, e), ascribed to the \( A_{1u} \) mode, which is IR-active. The appearance of this peak implies the breaking of the crystal symmetry in the third dimension due to the limited thickness and the presence of the interfaces.\(^{45,46}\)

Figure 5. (a-e) Raman spectra of as-deposited \( \text{Bi}_2(\text{Se}_{1-x}\text{Te}_x)_3 \) films with \( x \) ranging from 0 to 1. (f) phonon frequencies (orange: \( E_g^2 \) mode; green: \( A_{1g}^2 \) mode) as a function of Te composition. The inset provides the schematic diagrams for the two Raman-active modes.

LPCVD of \((\text{Bi}_1\text{Sb}_y\text{Te}_3)\) thin films

To ascertain the compatibility of the precursors required for the target ternary \((\text{Bi}_1\text{Sb}_y\text{Te}_3)\) thin films, various ratios of \([\text{MCl}_3(\text{Te}^\text{Bu}_2)_3](\text{M} = \text{Bi} \text{and Sb})\) were analysed by \(^{125}\text{Te}\{\text{H}\} \text{NMR spectroscopy in \text{CH}_2\text{Cl}_2}\). In all cases, just one Te resonance was observed, consistent with the Te \text{Bu}_2 ligands being labile and freely exchanging between the two weakly Lewis acidic MCl\(_3\) units. A gradual change in chemical shift is observed with increasing Bi content, from 237 ppm for pure \([\text{SbCl}_3(\text{Te}^\text{Bu}_2)_3])\), to 262 ppm for pure \([\text{BiCl}_3(\text{Te}^\text{Bu}_2)_3]\).

In order to deposit the target ternary \((\text{Bi}_1\text{Sb}_y\text{Te}_3)\) films, different ratios of the \([\text{BiCl}_3(\text{Te}^\text{Bu}_2)_3]\) and \([\text{SbCl}_3(\text{Te}^\text{Bu}_2)_3]\) precursors were combined. In a typical LPCVD experiment, ca. 60 mg total mass of the reagents were combined in the chosen ratio, and the deposition was performed at 500 °C onto SiO\(_2\) substrates, leading to silver-grey films.
across several substrates. Temperature profiling of the furnace revealed that when set to 500 °C, there was a temperature gradient from 270 °C at the edge of the furnace to 496 °C in the centre. Analysis of the films by XRD, EDX, SEM and Raman spectroscopy revealed that there was a variation in composition across the substrates, with increasing Sb content at higher deposition temperatures. The following analysis focuses on the films with the best coverage and showing a clear compositional variation with deposition temperature (across an 8 °C range from 474–482 °C), with the composition changing from Bi-rich at the cooler end, to Sb rich at the hotter end.

EDX analysis (Fig. 6a) was used to map the composition along the length of the sample (as a function of deposition temperature). Figure 6b shows the change in %Sb content with temperature across the substrate; moving from lower to higher temperature the Bi content decreases. It also shows that the Sb-rich phases deposit within a very narrow temperature range. It is clear that Bi₂Te₃ deposits more easily at lower temperatures than Sb₂Te₃ and consequently, the Bi content in the vapour phase of the precursor is depleted in the early stages of the hot zone, which means it does not reach the substrates at higher temperatures.

![Figure 6: (a) EDX spectra and (b) relationship between (Bi₁₋ₓSbx)₂Te₃ film composition and the increasing temperature of deposition (indicating the temperatures at positions A, B and C).](image)

SEM images (Fig. 7) taken at three positions (A-C) across the substrate show that the morphology is rather different from the regular hexagonal morphology observed for either Bi₂Te₃ or Sb₂Te₃. Moving along the substrate to the more Sb-rich phase, individual irregular-shaped plate-like crystallites are observed, rather than regular hexagons.

![Figure 7: SEM images of three regions (A-C) of the film deposited from a 1:1 ratio of [SbCl₃(TenBu₂)₃] and [BiCl₃(TenBu₂)₃], together with the binary phases (Sb₂Te₃ and Bi₂Te₃).](image)

Figure 8: (a) Grazing incidence XRD patterns from 3 positions (A-C; Sb poor to Sb rich) of a ternary sample deposited from a 1:1 ratio of [SbCl₃(TeBu₂)₃] and [BiCl₃(TeBu₂)₃], together with the binary phases (Sb₂Te₃ and Bi₂Te₃). Position A: a = 4.370(11) and c = 30.80(8) Å, Position B: a = 4.327(8) and c = 30.54(8) Å, Position C: a = 4.249(9) and c = 30.29(8) Å. (b) expanded XRD patterns showing the systematic shift of the 015 peak; (c) refined lattice parameters as a function of the Sb content for different as-deposited (Bi₁₋ₓSbx)₂Te₃ films. The composition of the film was also mapped with Raman spectroscopy (Fig. 9). This shows the shift in peaks from Bi₂Te₃ to Sb₂Te₃. The E₂g vibrational mode shifts from 100 to 120 cm⁻¹ and the A¹g mode shifts from 134 to 167 cm⁻¹ showing the change in composition of the solid solution of the ternary phase. This is consistent with Raman spectra of (Bi₁₋ₓSbx)₂Te₃ deposited by solvothermal synthesis and MBE.

![Figure 9: (a-e) Raman spectra from 3 positions (Sb poor to Sb rich) of a ternary (Bi₁₋ₓSbx)₂Te₃ sample deposited from a 1:1 ratio of [SbCl₃(TeBu₂)₃] and [BiCl₃(TeBu₂)₃], together with the binary phases (Sb₂Te₃ and Bi₂Te₃); (f) phonon frequencies (orange: E₂g mode; green: A¹g mode) as a function of Sb composition. The inset provides the schematic diagrams for the two Raman-active modes.](image)

Conclusions

This work presents a chemically compatible library of molecular precursors suitable for the LPCVD growth of high quality binary M₂E₃ (M = Sb, Bi; E = Se, Te) thin films on silica. Moreover, their suitability to be combined in different ratios, producing rapidly scrambling precursor systems, allows a highly innovative route for the LPCVD of the key ternary Bi₂(Se₁₋ₓTex)₃ and (Bi₁₋ₓSbx)₂Te₃ films with very good compositional, structural and morphological control, as well-distributed solid solutions (following Vegard behaviour). In the case of Bi₂(Se₁₋ₓTex)₃, the ternary composition is mainly governed by the relative ratios of the precursors used, whilst for (Bi₁₋ₓSbx)₂Te₃ the deposition temperature has a greater influence on the film composition.

Good compositional, structural and morphological control across the ternary phase is very important for tuning the functional properties of the V-VI materials for applications in thermoelectric devices or...
topological insulators. This, coupled with the demonstration that our precursor system allows selective film growth onto defined regions of lithographically patterned substrates, suggests that using these new precursors in a CVD based approach offers exciting prospects for the fabrication of thin film micro-thermoelectric generators. This will form the basis of our future work.

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Conflicts of interest
There are no conflicts to declare.

Notes and references
‡ Methods for the precursor syntheses and characterisation, LPCVD experiments and film characterisation are presented in the ESI.

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