**Low pressure CVD of GeE (E = Te, Se, S) thin films from alkylgermanium chalcogenolate precursors and effect of the deposition temperature on the thermoelectric performance of GeTe**

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**Keywords**

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**Abstract**

The homologous series, [GenBu3(EnBu)] (E = Te, Se, S; **(1)**, **(3)** and **(4)**) and [[GenBu2(TenBu)2] **(2)** have been synthesized as mobile oils in excellent yield (72-93%) and evaluated as single source precursors for the low pressure chemical vapor deposition (LPCVD) of GeE thin films on silica. Compositional and structural characterization of the deposits have been performed by grazing incidence X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis and Raman spectroscopy, confirming the phase purity and stoichiometry. Electrical characterization via variable temperature Hall effect measurements are also reported. Given the strong interest in GeTe and its alloys for thermoelectric applications, variable temperature Seebeck data were also investigated for a series of p-type GeTe films. The data show that it is possible to tune the thermoelectric response through intrinsic Ge vacancy regulation by varying the deposition temperature, with the highest power factor (40 μW/K2cm @629 K) and effective *ZT* values observed for the films deposited at higher temperatures.

1. Introduction

The germanium monochalcogenides, GeE (E = Te, Se, S) constitute a very interesting family of layered semiconductor materials with band gaps of 0.6, 1.33 and 1.60 eV, respectively, attracting attention for a wide range of potential applications in low power electronics and thermoelectrics. Among this family, GeTe has attracted most research endeavor because of its high electrical conductivity, reversible amorphous–crystalline phase transition behavior and its applications for solid state memory.[[1]](#endnote-1),[[2]](#endnote-2),[[3]](#endnote-3) The two lighter congeners, GeS and GeSe, are also of interest for photovoltaic devices, while GeS has attracted consideration as a battery material.[[4]](#endnote-4),[[5]](#endnote-5),[[6]](#endnote-6),[[7]](#endnote-7)

Recently, the germanium monochalcogenides have also received emergent attention as thermoelectric materials.[[8]](#endnote-8) Thermoelectric technology enables direct conversion between heat and electricity and has been considered as a clean and sustainable technology for power generation.[[9]](#endnote-9) It offer maintenance-free, solid-state operation, as well as very good reliability and a long operational lifetime. The conversion efficiency for power generation essentially requires thermoelectric materials that exhibit a high dimensionless figure-of-merit (), where is the Seebeck coefficient, denotes the electrical conductivity, is the temperature (in Kelvin), represents the thermal conductivity which contains contribution from electrons () and phonons (). Larger values can be achieved by improving the power factor (), while also reducing the thermal conductivity.[[10]](#endnote-10) Significant effort has been devoted to developing thermoelectric materials with *ZT* values in different temperature regimes.[[11]](#endnote-11) SiGe alloys and half-Heusler are strong candidates for high temperature applications, while Bi2Te3 based chalcogenides are among the best known materials for near-room-temperature applications, and PbTe-based alloys for mid-temperature applications.[[12]](#endnote-12),[[13]](#endnote-13) GeTe has demonstrated outstanding thermoelectric performance especially in the temperatures range 500-800 K. This makes it a promising candidate to replace the conventional Pb-based chalcogenide (e.g. PbTe) whose mass-market application is hindered by its toxicity.8

GeTe has been shown to be fabricated into both bulk and thin film forms through a variety of different techniques. These include high-temperature melting,[[14]](#endnote-14) spark plasma sintering (SPS)[[15]](#endnote-15),[[16]](#endnote-16) and solid-state reactions.[[17]](#endnote-17),[[18]](#endnote-18) In addition, deposition of thin film GeTe has also been reported using sputtering,[[19]](#endnote-19),[[20]](#endnote-20) thermal evaporation,[[21]](#endnote-21) molecular beam epitaxy,[[22]](#endnote-22) and pulsed laser deposition.[[23]](#endnote-23),[[24]](#endnote-24) Chemical vapor deposition (CVD) can produce thin films with superior quality compared to those from sputtering techniques in terms of conformity, coverage and stoichiometry control. Conventionally in CVD, deposition of binary GeTe uses dual precursors, which require careful control to obtain high quality stoichiometric thin films.[[25]](#endnote-25) As an alternative solution, single source precursors can provide much easier handling and high atom efficiency for the CVD process. In addition, properties such as stoichiometry, morphology and area selectivity of the target material can be directly controlled in the precursor design. We have previously demonstrated the deposition of a range of high-quality binary (e.g. SnSe2, TiSe2, Bi2Te3 and Sb2Te3) and ternary (e.g. Bi2(Se1-xTex)3 and (Bi1-ySby)2Te3) chalcogenide materials *via* single source precursors.[[26]](#endnote-26),[[27]](#endnote-27),[[28]](#endnote-28),[[29]](#endnote-29),[[30]](#endnote-30),[[31]](#endnote-31)

Only a small number of single source precursors for the deposition of GeTe thin films and the formation of GeTe nanoparticles have been reported previously. The benefits of using a single source precursor include fine control over the stoichiometry, as this is designed into the precursor. These precursors include: (R2GeTe)3, where R is Et or Bu, as described by Gupta *et al.* for the thermal decomposition synthesis of GeTe nanoparticles;[[32]](#endnote-32) Some often quite elaborate species, including [Ge({N(Me2SiCH2CH2Me2Si)}2iPr(TeiPr)] used in the metal organic CVD of GeTe thin films by Chen *et al*.;[[33]](#endnote-33) [Ge(Me2NCH2CMe2O)2S] and [Ge(Me2NCH2CMe2S)2E] (where E is Se or Te) described for the thermal decomposition synthesis of GeE by Kim *et al.*;8 [Ge(S2COR’)4] (R’=Et or iPr) and [nBu2Ge(S2COiPr)2] described by Shah *et al.* for the thermolysis of GeS;[[34]](#endnote-34) and the use of [Ge(TenBu)4] in LPCVD described in our previous work.[[35]](#endnote-35) These precursors are unsuitable for a large number of deposition techniques due to their high molecular weights and low volatilities, as well as poorly defined thermal decomposition pathways, or, in the case of [Ge(TenBu)4], the unbalanced stoichiometry, which leads to some contamination by excess tellurium.

In the present study, we report the preparation and characterization of the novel single source precursors, [GenBu3(TenBu)] (**1**) and [GenBu2(TenBu)2] (**2**), together with the lighter congeners, [GenBu3(EnBu)] (E= Se (**3**), S (**4**)), and their utilization for the controlled growth of single phase GeE thin films by LPCVD onto silica substrates. The resultant films demonstrate high purity and the thermoelectric properties of the GeTe films are competitive with the state-of-art values. We also present temperature-dependent thermoelectric properties (Seebeck coefficient, electrical conductivity, carrier concentration and mobility) for the GeTe films, demonstrating a highly competitive performance. Moreover, an effective strategy for improving power factor to achieve high power factor values is by tuning the carrier concentration and using our CVD approach we also demonstrate the capability of tuning the thermoelectric performance by modifying the CVD conditions, i.e. by optimizing the deposition temperature, the p-type GeTe thin films demonstrate significantly improved thermoelectric properties, with maximum power factor of 40 μW/K2cm achieved at 629 K.

1. Materials and methods
   1. Single source precursor synthesis

The syntheses of the target used a dry N2 atmosphere and employed Schlenk and glove box techniques. THF and hexane solvents were distilled from sodium wire immediately before use, while NMR solvents were stored over molecular sieves in the glove box. The nBu3GeCl and nBu2GeCl2 were obtained from Alfa, while the nBuSH, Se and Te pellets were purchased from Sigma. 1H, 13C{1H}, 77Se{1H} and 125Te{1H} NMR spectra were recorded at room temperature using a Bruker AV400 spectrometer in CDCl3 and referenced against residual solvent signals (1H and 13C{1H}) or against external neat SeMe2 or TeMe2 (77Se and 125Te, respectively). Elemental analyses were undertaken by Medac Ltd.

The thermal properties of the new precursor compounds were explored by TGA, using *ca.* 10-20 mg of each compound, which was transferred into an Al2O3 crucible inside a dry, N2-purged glove box before moving into the TGA instrument which was under flowing argon. The temperature of the sample was increased at a rate of 5 °C min-1 under flowing Ar, across the range 30–600 °C and the mass loss was monitored simulataneously (SI Figs. S6-S9).

**[GenBu3(TenBu)] (1):** Tellurium granules (0.297 g, 2.33 × 10-3 mol) were ground to form a fine powder in the glovebox before being suspended in THF (20 mL) and then cooling to 77 K (liquid N2), at which point nBuLi solution in hexanes (1 mL, 1.60 × 10-3 mol) was added dropwise. After thawing, the solution was stirred, at which point it turned yellow and then red. A further aliquot of nBuLi solution (0.5 mL, 8.0 × 10-4 mol) was added dropwise until a light yellow color remained. A solution of nBu3GeCl (0.651 g, 2.33 × 10-3 mol) in THF (20 mL) was then added dropwise. The reaction mixture was then refluxed to 90 °C and allowed to stir for 24 h, forming an amber solution. After cooling the solution, the volatiles were removed *in vacuo* and hexane (30 mL) was added, causing the solution to turn cloudy (due to precipitation of the LiCl by-product). The mixture was filtered by cannula filter before removing the volatiles under vacuum, washing with further hexane (30 mL) and then taken to dryness under vacuum, leaving an orange-red oil. Yield 0.836 g, 84 %. Elemental analysis: calc. for C16H36GeTe (428.77 gmol-1): C 44.83, H 8.46 %. Found: C 44.05, H 8.07 %. 1H NMR (CDCl3): δ/ppm = 0.90 (two overlapping t, *J* = 8.00 Hz, [12H], CH3) 1.11 (t, [6H], GeCH2) 1.36 and 1.40 (overlapping tq, tq and t, [14H], CH2) 1.65 (tq, [2H], CH2) 2.47 (t, [2H], TeCH2). 13C{1H}NMR (CDCl3): δ/ppm = -5.51 (CH2), 13.31 (CH2), 13.70 (CH3), 16.68 (CH2), 25.01 (CH2), 26.02 (CH2), 28.32 (CH2), 36.37 (CH2). 125Te {1H} NMR (CDCl3): δ/ppm = -400.1 (s).

**[GeBu2(TeBu)2] (2):** Method as described above, but using tellurium granules (2.1784 g, 1.71 × 10-2 mol), nBuLi solution in hexanes (11 mL) and nBu2GeCl2 (2.000 g, 7.76 × 10-3 mol). Orange oil. Yield 4.001 g, 93%. Elemental analysis: calc. for C16H36GeTe2 (556.47 gmol-1): C 34.55, H 6.52 %. Found: C 34.52, H 6.51 %. 1H NMR (CDCl3): δ/ppm = 0.89 (two overlapping t, *J* = 8.00 Hz, [12H], CH3), 1.37-1.49 ( two overlapping tt and two tq, [16H], GeCH2 and CH2), 1.69 (overlapping t quart, [4H], CH2), 2.58 (t with overlapping 125Te satellites, [4H], TeCH2). 13C{1H}NMR (CDCl3): δ/ppm = 1.97 (1J125Te13C = 138 Hz, CH2), 13.34 (CH3), 13.58 (CH3), 21.52 (CH2), 25.01 (CH2), 25.29 (CH2), 29.36 (CH2), 35.55 (3J125Te13C = 16 Hz, CH2). 125Te{1H} NMR (CDCl3): δ/ppm = ‑294.9 (s).

**[GenBu3(SenBu)] (3)**: Selenium granules (0.229 g, 2.89 × 10-3 mol) were ground into a fine powder under an N2 atmosphere (glove box) before being suspended in THF (20 mL). After freezing the solution to 77 K (liq. N2), nBuLi solution in hexanes (1.1 mL, 1.76 × 10‑3mol) was added dropwise before the mixture was allowed to thaw. Upon stirring the solution turned pale yellow initially and then deepened to a red colour. Further nBuLi solution (0.6 mL, 9.64 × 10‑4mol) was then added dropwise until the pale-yellow color persisted. nBu3GeCl (0.735 g, 2.63 × 10‑3mol) in THF (20 mL) was then added dropwise and the reaction mixture was refluxed (85 °C) with stirring for 12 h. After cooling the yellow solution, the solvent was removed *in vacuo* and hexane (30 mL) was added, causing the LiCl by-product to precipitate. This was removed by cannula filtration and the remaining filtrate was evaporated to dryness *in vacuo*, washed with further hexane (30 mL) and dried under vacuum, to produce a yellow oil. Yield 0.767 g, 77 %. Elemental analysis: calc. for C16H36GeSe (380.03 gmol-1): C 50.57, H 9.55 %. Found: C 51.11, H 9.67 %. 1H NMR (CDCl3): δ/ppm = 0.89 (two overlapping t, *J* = 8.00 Hz, [12H], CH3) 1.04 (t, [6H], GeCH2) 1.29 - 1.46 (overlapping tt, qt and tt, [14H] CH2), 1.62 (tq, [2H], CH2) 2.47 (t with overlapping 77Se satellites, [2H], SeCH2). 13C {1H} NMR (CDCl3): δ/ppm = 13.50 (CH3), 13.65 (CH2), 16.18 (CH3), 17.36 (CH2), 22.95 (CH2), 26.11 (CH2), 27.43 (CH2), 35.53 (CH2). 77Se {1H} NMR (CDCl3): δ/ppm = -144.8 (s).

**[GenBu3(SnBu)] (4):** To a solution of sodium metal (0.076 g, 2.52 × 10-3 mol) in anhydrous ethanol (15 mL) was added butane thiol (0.227 g, 2.52 × 10-3 mol) and the reaction mixture was stirred for 2 h forming a colorless solution. The volatiles were then removed *in vacuo*, depositing a white powdered solid which was then suspended in THF (15 mL) and a solution of tributylgermanium chloride (0.704 g, 2.52 × 10-3 mol) in THF (15 mL), was added dropwise over 5 min., to form a clear reaction mixture, which was stirred for 1 h before being refluxed at 70 °C. The resulting cloudy reaction mixture was then concentrated *in vacuo* and washed with hexane (15 mL) before being filtered. After removal of the solvent, the colorless oil was washed with dry hexane (20 mL) and dried under vacuum. Yield: 0.607 g, 72%. Elemental analysis: calc for C16H36GeS (333.12 g mol-1). C 57.69, H 10.89 %. Found: C 57.54, H 10.93 %. 1H NMR (CDCl3): δ/ppm = 0.90 (t, *J* = 8.00 Hz, [12H], CH3) 1.01 (t, [6H], CH2) 1.35-1.42 (two tq and a tt, [14H], CH2), 2.47 (t, [2H], CH2) 3.65 (t, [2H], CH2). 13C {1H} NMR (CDCl3) δ/ppm = 13.62 (CH3), 13.67 (CH3), 15.72 (CH2), 21.89 (CH2), 26.19 (CH2), 26.26 (CH2), 27.06 (CH2), 35.61 (CH2).

* 1. LPCVD onto fused quartz substrates

Before use, the fused quartz substrates were prepared by washing with deionized water, followed by ethanol and then drying thoroughly in an oven. Typically, the precursor (5-50 mg) and substrates were loaded into a closed ended quartz tube within a glove box. The precursor was then carefully introduced into the precursor bulb at the other end of the tube via a syringe, before the substrate tiles were placed lengthways end-to-end (usually between 0 to 4 cm away from the precursor bulb) in the CVD tube. The tube was then placed horizontally into the furnace and positioned so that the precursor bulb was protruding from the furnace, before evacuating the tube to 0.01 - 0.40 mmHg (0.01 – 0.40 Torr). The furnace was then heated to the requisite temperature (using the TGA data as a guide) and allowed to stabilize. In this study the furnace temperature settings were 550-650 ˚C (GeTe), 600 ˚C (GeSe) and 700 ˚C (GeS); with the higher temperatures required for the lighter chalcogens most likely a consequence of the higher stability of the Se-C and S-C bonds in (**3**) and (**4**) compared to the Te-C bonds in (**1**) and (**2**). At lower temperatures no GeSe or GeS films were observed.

The tube was positioned so that the precursor was sufficiently close to the heated region for evaporation to occur and this position was then maintained for 5-10 mins. until all of the precursor had vaporized. After the deposition was complete, the tube was removed from the furnace, cooled to room temperature and then transferred to the glovebox, before the substrates were removed and stored for characterization.

These experiments formed continuous reflective silver films of GeTe, grey films of GeSe, each with coverages of *ca*. 1 cm2, and grey/black GeS films with lower coverage.

* 1. Thin film characterization

Scanning electron microscopy (SEM) experiments used a Zeiss EVO LS 25 with an accelerating voltage of 10 kV, and energy-dispersive X-ray (EDX) analysis were obtained from an Oxford INCAx-act X-ray detector. Raman spectra from the thin film deposits were measured at room temperature using a Renishaw InVia micro Raman spectrometer fitted with a He-Ne laser (wavelength = 633 nm) with an incident laser power of *ca.* 1 mW in each case.

Grazing incidence X-ray diffraction (XRD) patterns were collected using a Rigaku SmartLab system with a Hypix detector, using Cu-Kα radiation with a 2θ scan range from 10 – 80o and a 1° ω-offset. The crystalline phase of the deposited material was determined by comparison with an XRD pattern from the Inorganic Crystal Structure Database (ICSD),[[36]](#endnote-36) and lattice parameters were refined by optimization of the fit using PDXL.[[37]](#endnote-37)

Variable temperature electrical characterization was undertaken using the Nanometrics HL5500PC Hall effect system to determine resistivity, carrier concentration () and in-plane mobility () using a van der Pauw method. Measurements were conducted in a range between 125 K to 450 K at 25 K step under a magnetic field of 0.5 T. Probes were ensured to be appropriately in contact with samples before each measurement. I-V curves were also recorded before each measurement to ensure Ohmic conduction as well as to optimize current for maximized voltage signal. Variable temperature Seebeck coefficient and electrical resistivity were measured using a commercial JouleYacht thin-film thermoelectric parameter test system (MRS-3L). The system was calibrated using a nickel foil reference standard and the measurement accuracy was found to be within 5%. Seebeck coefficients were determined using the differential method with a maximum temperature difference of 10 K. The resistivity was corrected for geometric error using the results from the Hall measurement system.

1. Results and Discussion
   1. Single source precursor synthesis and thermogravimetric evaluation

The germanium(IV) precursors (**1**)-(**4**) (Scheme 1) were identified as potential candidates for the growth of the germanium monochalcogenides, GeE (E = Te, Se, S), as they incorporate direct bonds between the Ge and E atoms, have sufficient volatility to allow vaporization in the CVD reactor and contain n-butyl groups that can readily undergo elimination reactions, leading to clean deposition of the target binary semiconductor. The target compounds **(1)**-**(4)** were isolated in very good yields as mobile oils using slightly modifications of the methods developed for [Bu3Sn(EBu)] (E = Te, Se, S), which we have shown to be effective precursors for the LPCVD growth of SnE thin films.[[38]](#endnote-38),[[39]](#endnote-39) The synthesis of the selenolate and tellurolate precursors (**1**-**3**) require a different synthetic route to that of (**4**). For the latter, a range of thiols are widely available commercially and simple deprotonation and salt elimination, as illustrated in Scheme 1 (bottom), yields the target thiolate precursor, (**4**). In contrast, selenols (RSeH) and tellurols (RTeH) are much less readily available, less stable and more toxic than thiols, and hence the insertion of elemental Se or Te into nBuLi to obtain the selenolate or tellurolate ions directly is much preferred, as shown in Scheme 1 (top). Precursors **(1)**-**(4)** are readily hydrolyzed, but can be handled briefly in air and are stable for several months when stored under an inert atmosphere. Their purity was confirmed by a combination of NMR spectroscopic data (1H, 13C{1H}, 77Se{1H} and 125Te{1H} – see SI Figs. S10-S22) and elemental analysis.



Scheme 1: Synthesis of precursors (**1**)-(**4**).

The TGA data (Figure 1, Table 1) indicate that the temperature associated with the onset of evaporation is lowest for **(3)** and **(4)**, *ca.* 200 ˚C, then **(1),** *ca.* 250 ˚C, before **(2)** at *ca.* 260 ˚C. From these experiments furnace temperatures were selected that would allow for the precursor bulb to reach the temperature needed for vaporization. Although the CVD experiments are performed at reduced pressure, while the TGA are performed at atmospheric pressure, the TGA data do provide a useful guide to whether a precursor may be suitable for LPCVD.

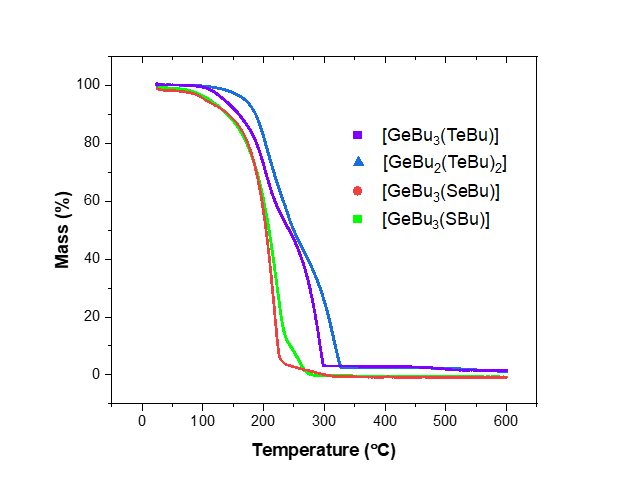


Figure 1 TGA data for precursors (**1**)-(**4**)

Table 1: Boiling points, Tvap, from the Sigma Aldrich material safety data sheet (for nBu4Sn) and estimated from the measured TGA data; enthalpy of vaporization calculated using the Clausius–Clapeyron equation, with reference values for nBu4Sn; entropy of vaporization calculated from ΔHvap/Tvap, together with reference values for nBu4Sn.

|  |  |  |  |
| --- | --- | --- | --- |
| **Compound** | Tvap  (K) | ΔHvap  (kJ mol-1) | ΔSvap  (J K-1 mol-1) |
| Bu4Sn\* | 518.15 | 69 ± 8 (61.3)30 | 137 ± 15 |
| **(1)** | 493.15 | 38 ± 8 | 77 ± 19 |
| **(2)** | 493.15 | 37 ± 8 | 75 ± 19 |
| **(3)** | 453.15 | 76 ± 17 | 169 ± 39 |
| **(4)** | 453.15 | 81 ± 18 | 178 ± 41 |

* 1. LPCVD of binary GeE films

*Morphological, compositional and structural properties of GeTe*

Figure 2(a)-(d) present the top-view SEM images of the four GeTe films deposited from **(1)** at temperatures ranging from 336 to 452 oC (measured by T profiling across the reactor furnace); good quality crystalline GeTe thin films could be produced reliably across this temperature range, enabling thorough characterization, including thermoelectric and electrical data to identify trends. All films display arrays of continuously interconnected polycrystalline films comprised of block-like grains with varying sizes. Cross sectional SEM analysis reveal that all film thicknesses are approximately 1 µm, as shown in Figure S1. EDX analysis of the four films also appear to be similar, revealing no significant impurities (Figure S2), and confirming the Ge : Te ratios are 51(2)% : 49(2)%.

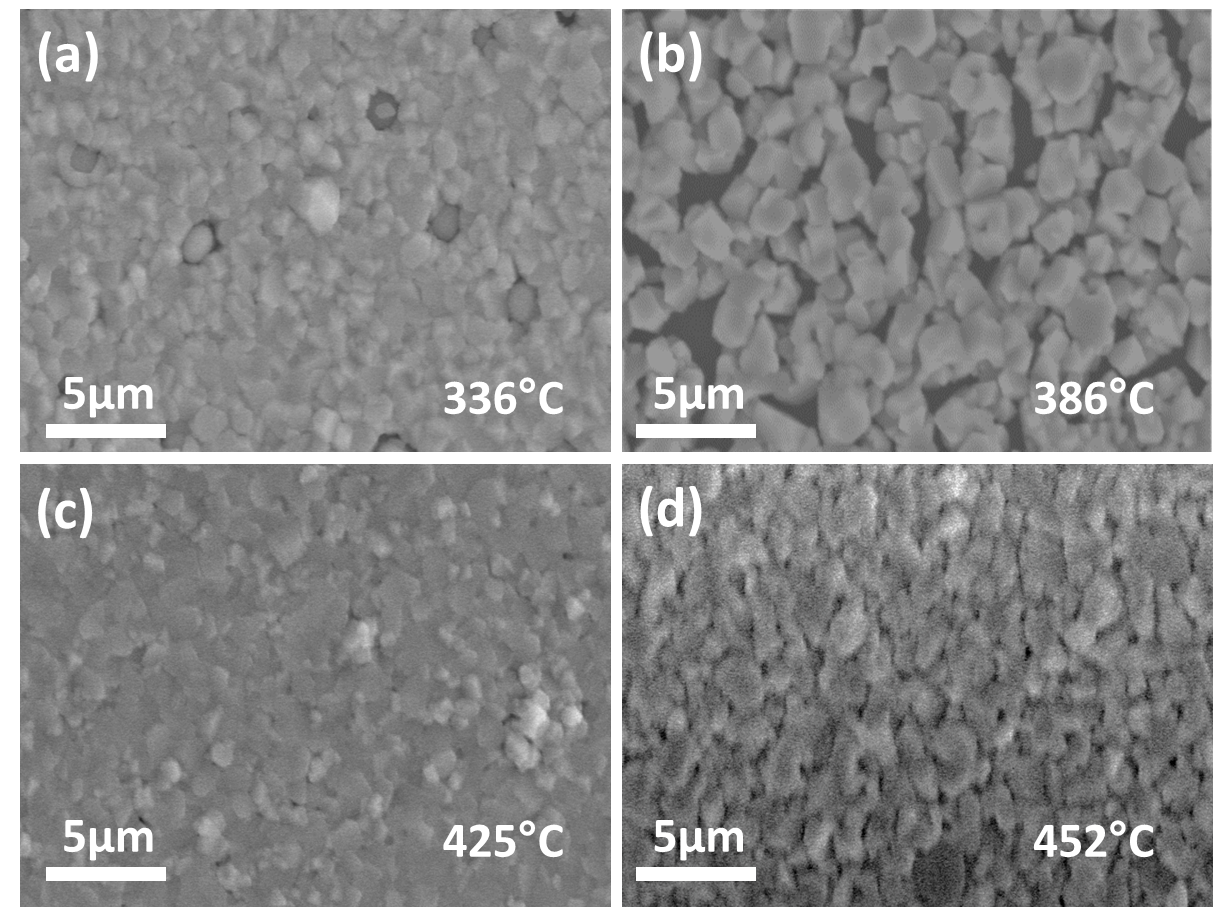


Figure 2 Top-view SEM images showing the morphologies of the GeTe films deposited by LPCVD at temperatures of (a) 336 °C, (b) 386 °C, (c) 425 °C and (d) 452 °C onto silica substrates.

Grazing incidence XRD analysis, as displayed in Figure 3a, confirms that all GeTe films deposited are rhombohedral GeTein the spacegroup of . This is in good agreement with literature from low temperature synthesis of GeTe.[[40]](#endnote-40) The lattice parameters (a, c) of all films are very similar, as shown in Figure 3b, and are well matched with the values reported in literature (a = b = 4.1519 and c = 10.710 Å).[[41]](#endnote-41) The XRD pattern from the Tdep = 425 °C sample shows some evidence fore preferred orientation, with enhancement of the 021 and 220 reflections and suppression of 202 reflection; the cause of this is not certain.

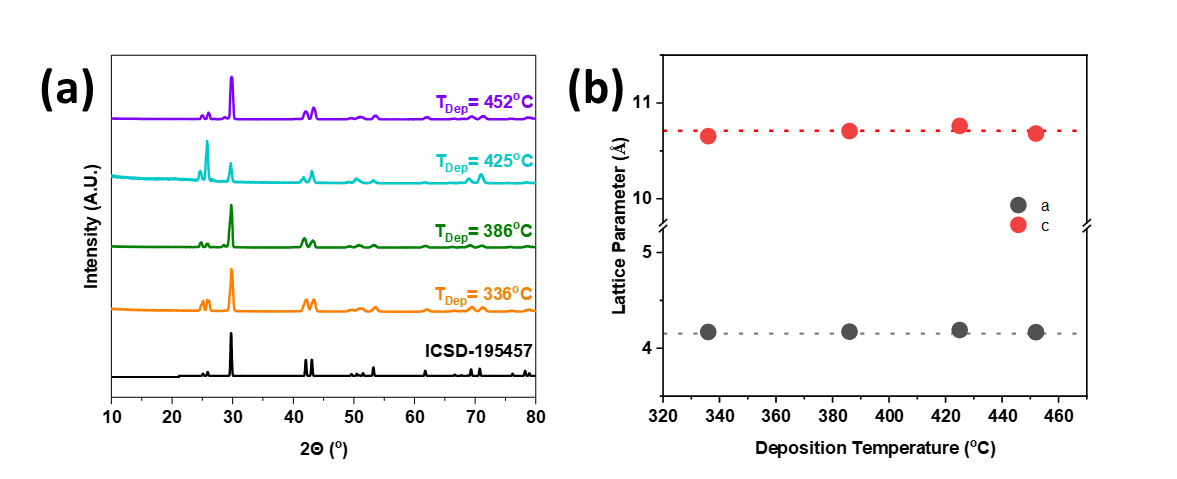


Figure 3 (a) XRD patterns of as-deposited GeTe films grown by LPCVD at a range of temperatures; (b) refined lattice parameters as a function of Tdep for the as-deposited GeTe films produced from precursor (**1**). The dotted lines represent the lattice parameter values from ref. 41.

Vibrational mode studies were conducted on these four films using Raman spectroscopy. The samples all displayed three peaks at similar positions, as shown in Figure 4a. The peak at *ca.* 125 cm-1 (black) is suggested to be related to the symmetric stretching vibrations of GeTe4 tetrahedra, commonly referred as the A1g mode.[[42]](#endnote-42),[[43]](#endnote-43) The peak at 140 cm-1 (blue peak) has been assigned previously to the aging of the sample,[[44]](#endnote-44),[[45]](#endnote-45) while the peak at 155 cm-1 (red peak) is due to vibrations of Ge atoms distinct from their distorted octahedral site.42,43 A red shift of the A1g peak can be observed with films deposited at higher temperature and is plotted in Figure 3b. Studies conducted by Kalra *et al* suggest that the shift is related to screening caused by free charge carriers.43 The abundance of the free charge carriers is correlated to the number of Ge vacancies found in our film. This implies that GeTe films deposited at higher temperature could result in more Ge vacancies due to the low vacancy formation energy of GeTe.43 Precursor (**2**) also produced polycrystalline GeTe films under similar conditions by LPCVD, with closely comparable structural, compositional and thermoelectric data (Figure S3).

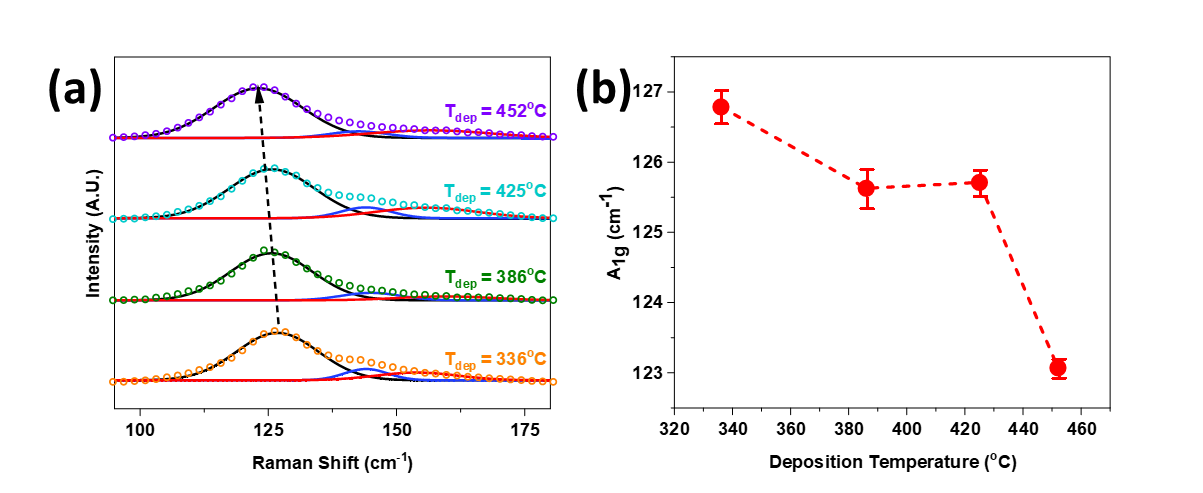


Figure 4 (a) The Raman spectra for GeTe thin films deposited from (**1**) at different temperatures, the open dotted curves are the Raman spectra while the black, blue and red curves represent the fitting of three vibration modes; (b) the peak positions of the A1g mode of the GeTe films as a function of deposition temperature.

* 1. LPCVD of GeSe and GeS

LPCVD experiments at 600 °C using precursor (3) gave grey films of GeSe with morphology as illustrated in Figure 5(a). The EDX analysis in Figure 5(b) shows no significant impurities, with the Ge:Se ratio determined to be 47% : 53%. Grazing incidence XRD analysis (Figure 5(c)) suggests the GeSe film is orthorhombic and the refined lattice parameters are a = 10.8089(7), b = 3.8222(2) and c = 4.3679(3) Å. This is in good agreement with the literature (a = 10.9208(4), b = 3.8708(3) and c = 4.4075(4) Å).[[46]](#endnote-46) The film demonstrates some preferred orientation, which is supported by the enhancement of the 002 and 004 reflections in the XRD pattern. Similar preferred orientation has also been seen in previous work on GeSe films deposited by thermal transport,[[47]](#endnote-47) and is common for these types of van der Waals materials. The Raman spectrum (Figure 5(d)) is also consistent with GeSe; the peak at 151 cm−1 corresponding to the B3g mode, and the 175 and 189 cm−1 peaks due to the Ag modes.[[48]](#endnote-48)

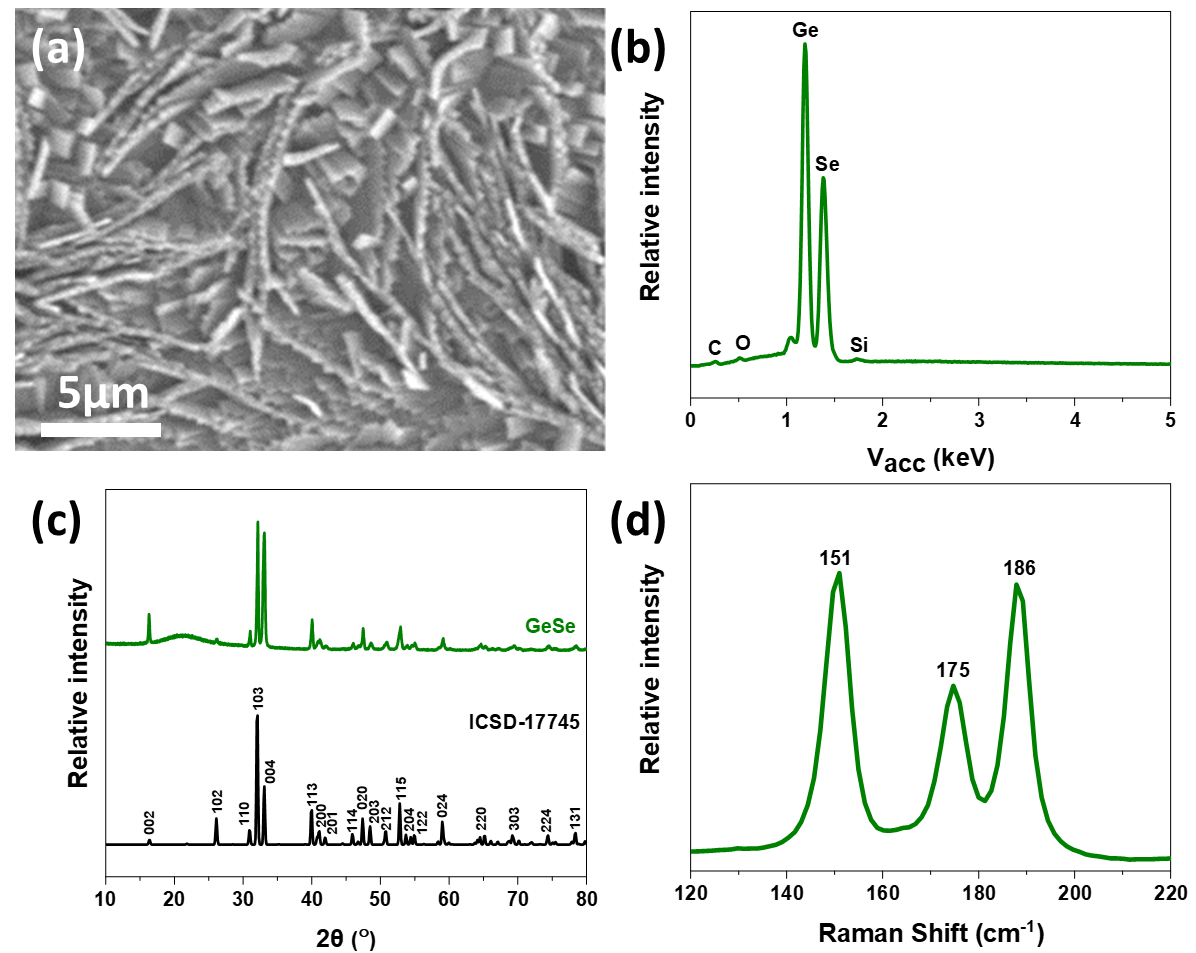


Figure 5: (a) Top view SEM image and (b) EDX spectrum of the GeSe thin film deposited from (**3**); (c) grazing incidence XRD pattern measured for GeSe deposited from **(3**) (green) and the matched literature pattern for bulk GeSe (black).46 The broad peak around 21° arises from the quartz substrate; (d) Raman spectrum of the GeSe thin film.

Similarly, using precursor (**4**) produced dark grey/black GeS thin films by LPCVD at a furnace temperature of 600 °C, although the coverage was less extensive than for the heavier chalcogenides. The SEM image in Figure 6(a) shows a film of GeS, formed of large /platelet crystallites. The EDX analysis (Figure 6(b)) shows the film is sulfur deficient with a Ge : S ratio of 54.8% : 45.2%. The grazing incidence XRD pattern displayed in Figure 6(c) (blue) matches well with the literature pattern for bulk orthorhombic GeS (black),[[49]](#endnote-49) with refined lattice parameters: a = 10.4661(5), b = 4.2792(2) and 3.63594(18) Å (literature: a = 10.470(2), b 4.297(1), c = 3.641(1) Å). The Raman spectrum, displayed in Figure 6(d), is also consistent with GeS; the peak at 211 cm−1 corresponds to the B3g mode, the 112, 239 and 267 cm−1 peaks are associated with the Ag modes.[[50]](#endnote-50)

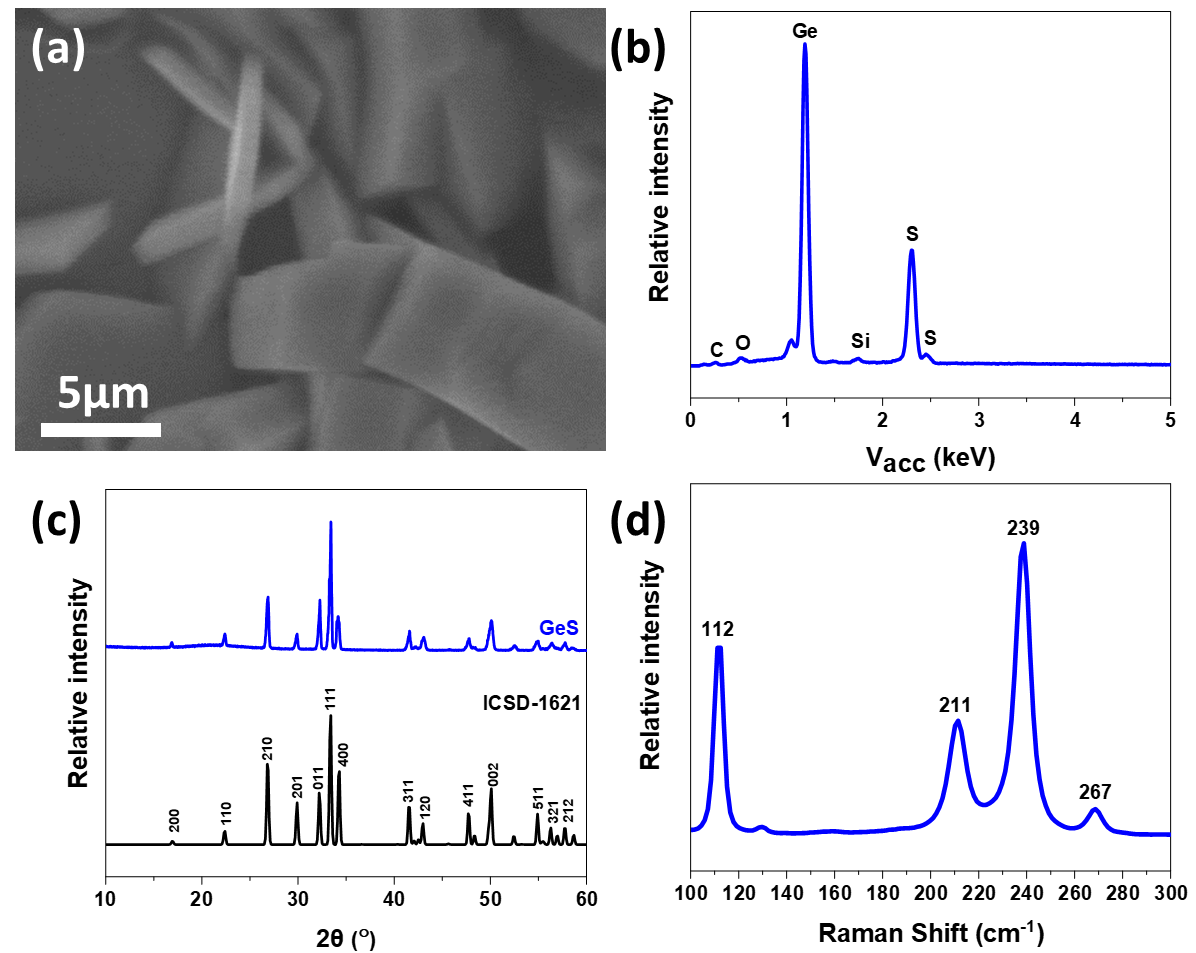


Figure 6 (a) Top-view SEM, and (b) EDX spectrum of the GeS film deposi5ed from (**4**); (c) grazing incidence XRD pattern for the GeS thin film (black) and the pattern from bulk GeS (black)49 (d) Raman spectrum of the same GeS film showing with Ag3, B3g, Ag1 and Ag2 stretches at 112, 211, 239 and 267 cm-1, respectively.

*3.4 Thermoelectric evaluation of GeTe films grown from (****1****):*

The high level of interest in GeTe as a thermoelectric material prompted a study to determine the thermoelectric performance of the GeTe thin films grown usingour CVD process. To this end*,* temperature dependent Seebeck measurements were performed. Precursor (**1**) was used for this study since it contains a 1:1 Ge : Te ratio and produced stoichiometric GeTe films reliably (whereas films from (**2**) sometimes also contained small amounts of elemental Te). Figure 7(a) presents the electrical conductivity of the four as-deposited GeTe films at a range of temperatures. It is clear that all films exhibit metallic-like electrical transport behavior as the conductivity reduces with increasing temperature. Additionally, significant variations of the electrical conductivity are observed for GeTe films deposited at different temperatures. To gain insight into the electrical transport mechanism of our GeTe films, temperature-dependent Hall measurements were made to determine the film carrier concentration and mobility. Figure 7(b) reveals that all GeTe films are *p*-type semiconducting with very high carrier concentrations of over 1021 cm-3. Such high carrier density results from the formation of a significant amount of Ge vacancies during the deposition process and is the main contributor to the high electrical conductivity exhibited by our GeTe films.[[51]](#endnote-51),[[52]](#endnote-52) It is also clear that the carrier concentration increases with increasing deposition temperature as suggested by the red shift of the A1g Raman peak in Figure 4(b). This implies the formation of Ge vacancies is further enhanced at higher temperature, suggesting our LPCVD approach is capable of tuning the film carrier concentration by controlling the deposition temperature. On the other hand, the Hall mobility is less dependent on deposition temperature, as shown in Figure 7(c). The overall mobilities for the four GeTe films are relatively low compared with the reported values in bulk GeTe.[[53]](#endnote-53) One limiting factor could be the strong electron scattering from the Ge vacancies. Figure 7(d) plots the film mobility as a function of the crystallite size obtained from the XRD data. It appears that the mobility of the GeTe films is governed by the size of the crystallites. Smaller crystallite sizes could lead to increased frequency of boundary scattering events, resulting in lower carrier mobility. This is consistent with the lowest mobility being observed for the GeTe film deposited at 425 °C. We note that the different crystallite orientation exhibited by this film (Figure 2(a)) may also contribute to the suppression of its mobility and electrical conductivity due to the anisotropic behavior of GeTe.[[54]](#endnote-54)

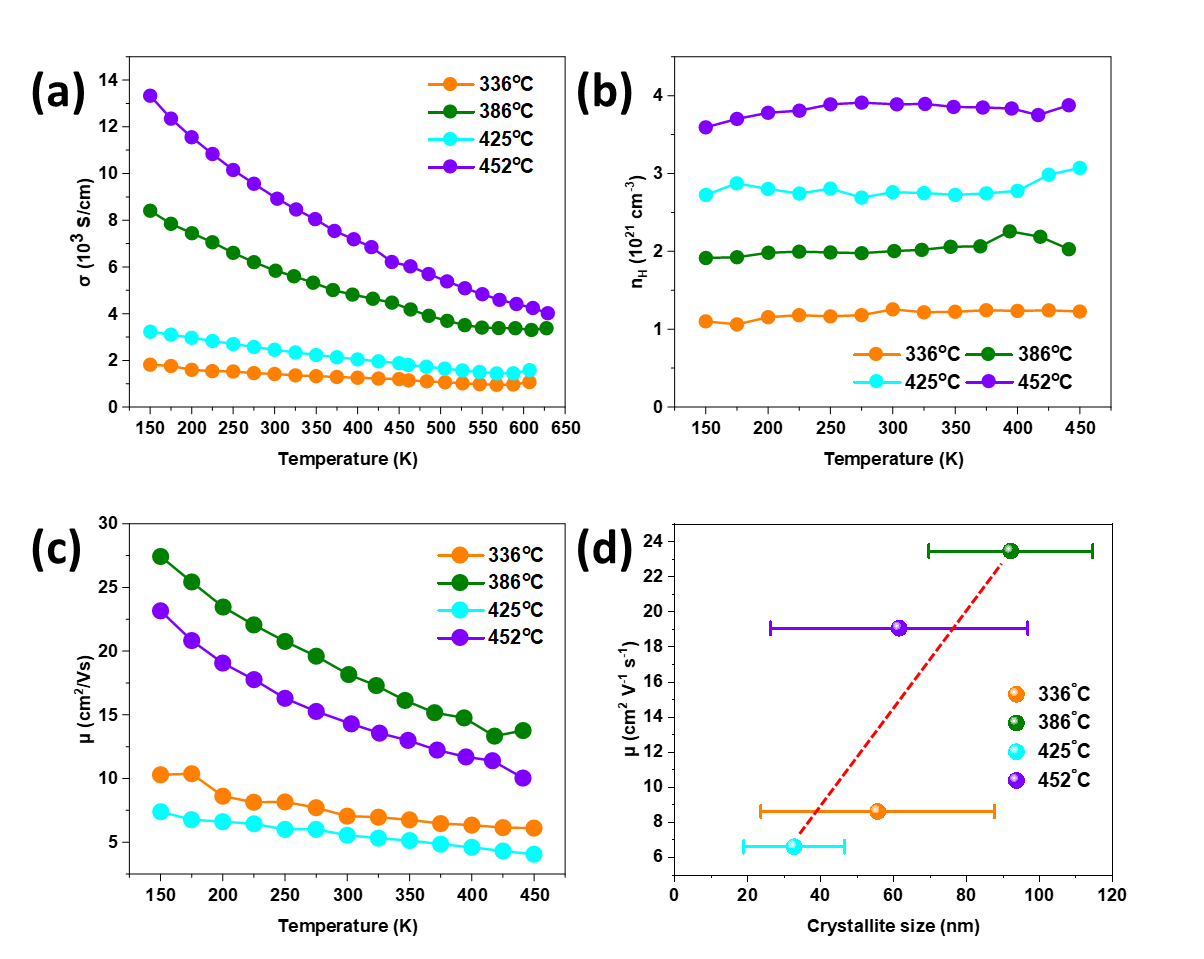


Figure 7 Temperature-dependent (a) electrical conductivity, (b) Hall carrier concentration, and (c) Hall mobility of the GeTe films deposited by LPCVD from (**1**) at different temperatures; (d) Room-temperature Hall mobility of the GeTe films as a function of crystallite size.

The temperature dependent Seebeck coefficients of GeTe thin films are displayed in Figure 8(a). The measurements confirm that all as-deposited GeTe films are *p*-type. However, unlike the electrical conductivity, the Seebeck values are less dependent on the deposition temperature and all four films are characterized by similar values. Figure 8(b) presents the Pisarenko plot of the GeTe films at 300 K. A simple electron transport model is used to calculate the dotted lines, which serve as guidelines. The model can be written as:

where is the Boltzmann constant, is the Planck constant, m\* is the effective mass, and are the carrier concentration and temperature, respectively. This equation assumes a degenerate semiconductor with a single parabolic band and energy-independent carrier scattering.9 The effective mass was found to increase with higher deposition temperature, suggesting the modification of the band structure.55 The similar Seebeck values observed from the different GeTe films is therefore a balance between the improvement brought by the increment of the effective mass and the deterioration resulting from the increasing carrier concentration. The power factors of the GeTe films can then be derived and are shown in Figure 8(c). Highly competitive power factor values are obtained from the films deposited at 452 and 386 °C, with a maximum value of 40 µW/cm·K2 achieved at 629 K. This is consistent with literature regarding high-quality pristine bulk GeTe samples and to the best of our knowledge is the highest presented for pristine GeTe in thin film form.[[55]](#endnote-55),[[56]](#endnote-56),[[57]](#endnote-57),[[58]](#endnote-58) Such competitive values obtained speaks to the high-quality nature of GeTe films produced from the single source precursor used in this work.

Reliable determination of the thermal conduction properties of thin films is very challenging and often prone to error. Here we estimate the total thermal conductivity by assuming a constant lattice contribution () of 0.5 W/mK. This is in-line with the values reported by others.54 The electrical part of the thermal conductivity () was calculated from the electrical conductivity by adopting the Wiedemann-Franz law (). The Lorenz number in the equation was calculated using empirical equation derived from the Seebeck coefficient proposed by Snyder et al.[[59]](#endnote-59) Unsurprisingly, is the dominating factor of the total thermal conductivity, as displayed in Figure S4. The estimated values are plotted in Figure 5d, showing a highest figure-of-merit of *ca.* 0.46 at 629 K. Thermoelectric properties of GeTe film deposited from precursor (**2**) were also investigated. The film was deposited at a temperature of 356 °C and demonstrate comparable performance to the films from precursor (**1**), as shown in Figure S5. The maximum power factor achieved is 26 µW/cm·K2 at 629 K.

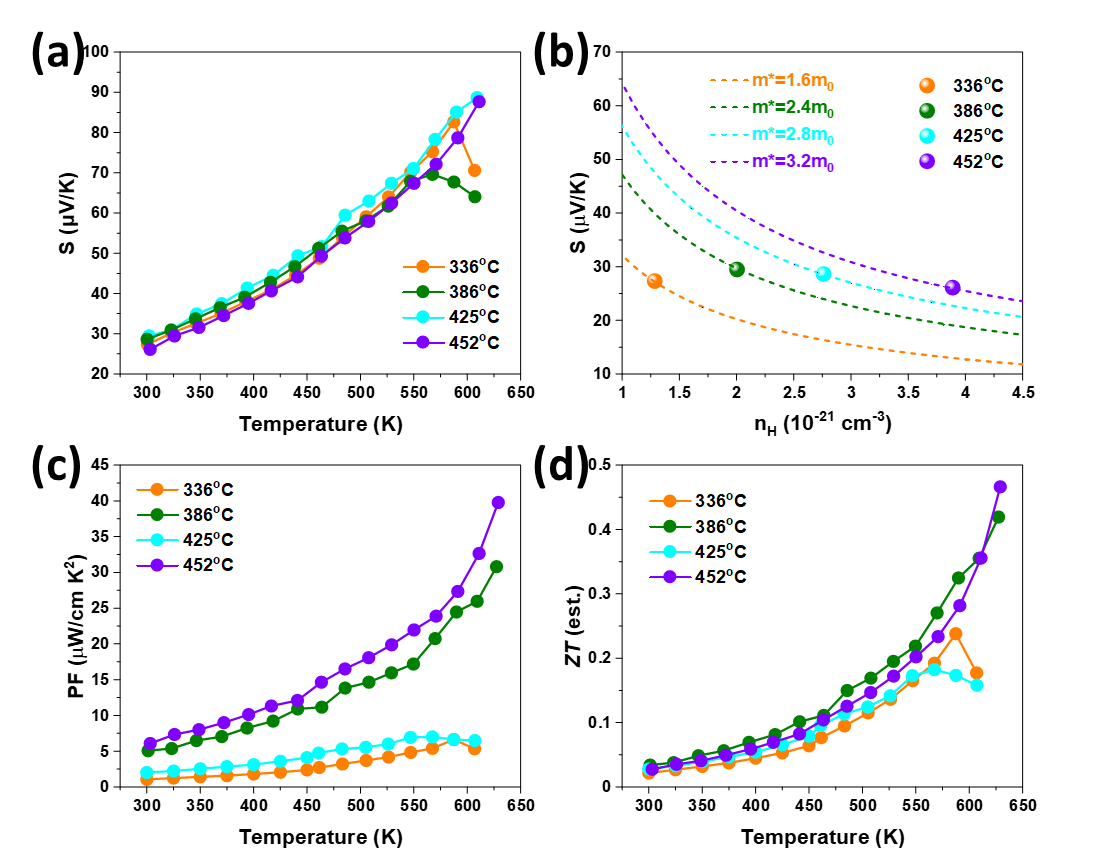


Figure 8 (a) Temperature-dependent in-plane Seebeck coefficient of the GeTe films deposited by LPCVD at different temperatures; (b) Pisarenko plot of the GeTe films at room-temperature; Temperature-dependent (c) in-plane power factors, and (d) estimated values of the the GeTe films deposited by LPCVD at different temperatures.

We note that the performance of our pristine GeTe is limited by its modest Seebeck coefficient and its high thermal conductivity (especially ), both of which have strong correlations with its high carrier concentration from inherent germanium vacancies. Further optimization of its carrier concentration is often obtained by substituting Ge with the group-15 elements (e.g. Sb and Bi).14,56 In addition, alloying with GeS and GeSe has also been proposed to be an effective way to improve its thermoelectric performance. The formation of a GeTe1-2xSexSx system introduces mass fluctuations and point defects which reduces the thermal conductivity, resulting in a significantly improved of 2.1.[[60]](#endnote-60) We have previously demonstrated the alloying of Bi2Te3 thin films with both Bi2Se3 and Sb2Te3 using our homologous single source precursors.30,[[61]](#endnote-61) This highlights other potential avenues to further optimize the thermoelectric properties of the GeTe films deposited in this work.

**Conclusions**

The homologous series of single source precursors, [GenBu3(EnBu)] (E = Te, Se, S), and [GenBu(TenBu)2], (**1**)-(**4**)), have been synthesized in good yields, fully characterized and their utility for the deposition of GeE thin films evaluated using LPCVD. The characterization of all the resulting films includes grazing incidence XRD, Raman spectroscopic data and SEM with EDX analysis. The GeE thin films produced are of good quality with little to no contamination, as shown by the EDX and Raman analysis.

Detailed thermoelectric measurements conducted on the GeTe thin films deposited using (**1**)indicate that the films are competitive with the literature data on bulk samples. Also identified is a correlation between the deposition temperature and the thermoelectric performance of the GeTe films. This effect could be exploited to further optimize the thermoelectric properties by adjusting the deposition temperature and mass of precursor to influence the grain size and electrical properties. Further optimization may also be possible by using a combination of precursor (**1**) or (**2**) with (**3**) and/or (**4**) to create ternary and/or quaternary alloys, leading to more profound changes in the band and crystal structures, and hence increasing the ZT value.

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**Conflicts of Interest**

The authors have no conflicts to declare.

**Supporting Information (SI)** includes SEM cross-sections and EDX spectra for the GeTe films from **(1)**; SEM, EDX, XRD and Raman data for the GeTe films from **(2)**; temperature dependent Lorentz number and total thermal conductivity for the GeTe films from **(1)**; temperature-dependent electrical conductivity, Hall carrier concentration and mobility, Seebeck coefficient and power factor of the GeTe films from **(2)**; isothermal TGA (Figs. S6-S9) and original NMR spectra (Figs. S10-S22) for **(1)**-**(4)**.

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