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Electronic Supplementary Information for:

Controlling the Nanostructure of Bismuth Telluride by Selective Chemical Vapour Deposition from a Single Source Precursor

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Substrate preparation: Sputtered SiO_2 and TiN substrates and photolithographically patterned TiN/SiO_2 substrates were prepared as described previously.[14] The E-beam lithography was carried out using a JEOL JBX-9300FS Electron beam Lithography System with a double-layered positive resist PMMA495. During exposure, the gun current was set to 4 nA with an accelerating voltage of 100 kV. The etching was performed by a RIE80+ with CHF_3 and Ar and the etch rate was found to be 0.37 nm s^{-1}.

Characterisation of nanocrystalline Bi_2Te_3: XRD measurements were carried out using a Rigaku Smartlab diffractometer with a 9 kW Cu-K_α source, parallel line focus incident beam and a DTex250 1D detector. Raman scattering spectra of the deposited films were measured at room temperature on a Renishaw InVia Micro Raman Spectrometer using a helium-neon laser with a wavelength of 633 nm. The incident laser power was adjusted to ~1 mW for all samples. SEM was performed using a Zeiss EVO LS 25 with an accelerating voltage of 10 kV, and EDX data were obtained with an Oxford INCAx-act X-ray detector, using a commercial sample of Bi_2Te_3 powder (Strem Chemicals, 99.99 %) as a reference. WDX was obtained with a ThermoFisher MagnaRay probe using NiC80 and PET X-ray diffracting crystals. High resolution SEM measurements were carried out with a field emission SEM (Jeol JSM 7500F) at an accelerating voltage of 2 kV. Microanalyses were undertaken by Medac Ltd. Hall effect measurements were performed at room temperature on a Nanometrics HL5500PC with a current of 1 mA under a field of 0.5 Tesla at 300 K. The Seebeck coefficient was determined using a custom-made Seebeck measurement unit, which was

calibrated against a polycrystalline Bi foil reference standard. The measurement accuracy was found to be within 5% and the system was calibrated using copper-constantan thermocouples and a high precision Keithley DMM 2000/E digital multimeter with 0.1% accuracy.

Thermogravimetric Analysis: Thermogravimetric analyses (TGA) used a Mettler Toledo TGA/SDTA851e analyser under a flow of Ar at 65 mL/min, contained within a dry, N_2-purged glove box. The temperature was increased at a rate of 10 ^{o}/min. TGA of [$BiCl_3(Te^nBu_2)_3$] shows that mass loss occurs in three distinct steps at 100−150 °C, 170−270 °C and 300−340 °C, leaving a residual mass of 37% which is unchanged up to 600 °C (Fig. S1), with a shiny residue being observed in the crucible. This suggests a complex decomposition pathway, with Bi_2Te_3 being the final residue (theoretical residual mass = 38%). The TGA also indicates limited reagent evaporation occurs at ambient pressure.

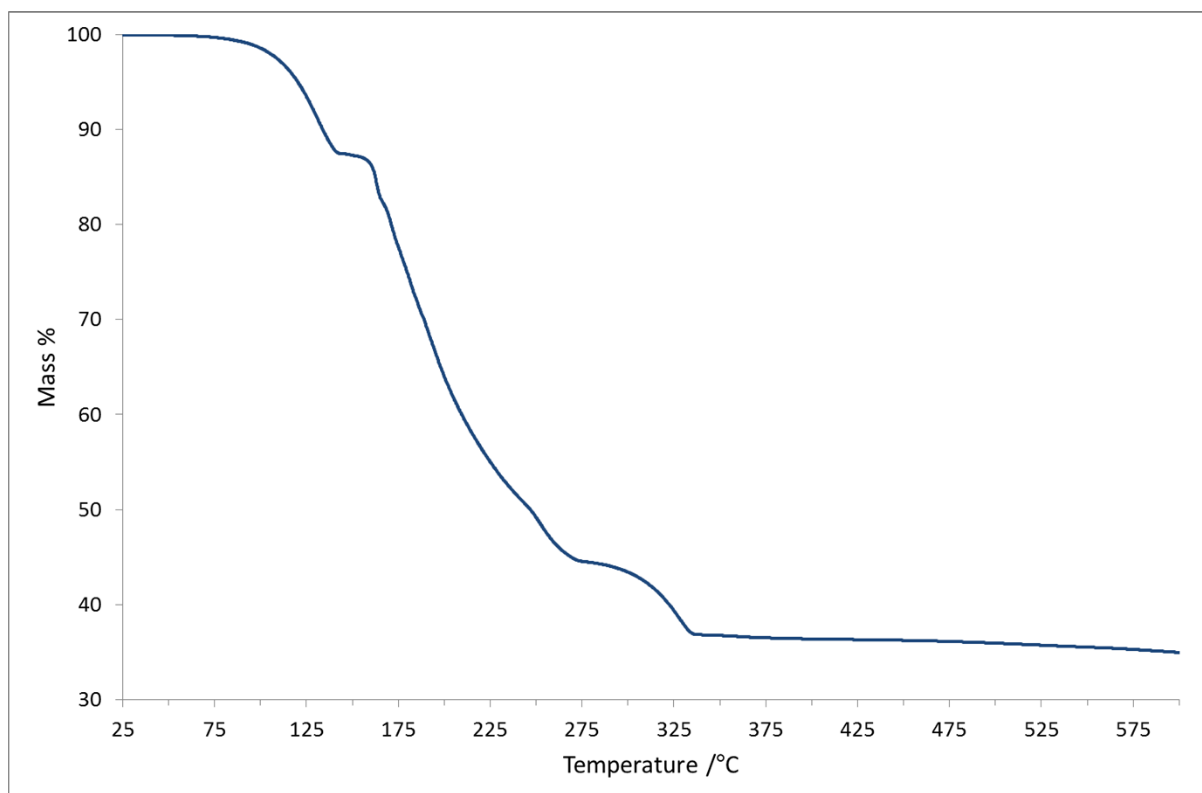
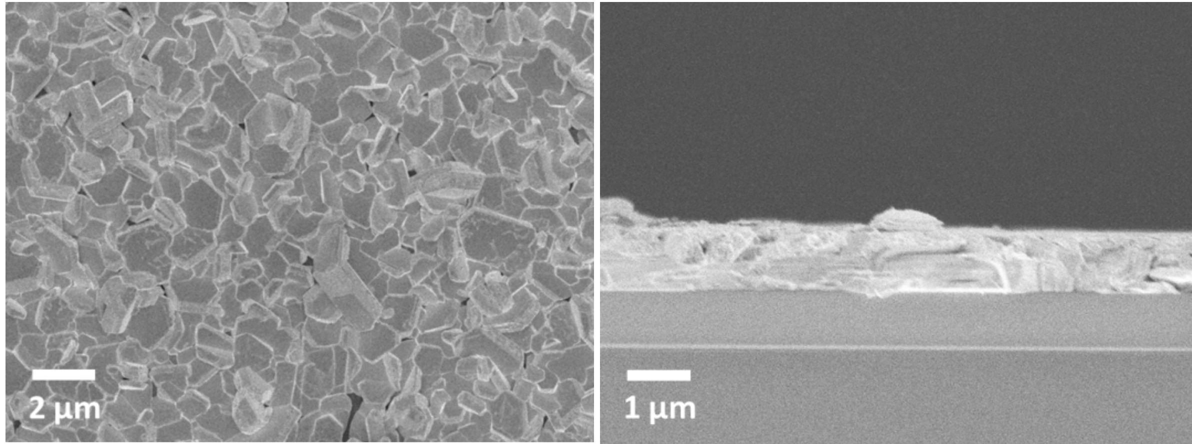


Figure S1. TGA plot for [$BiCl_3(Te^nBu_2)_3$] collected under Ar with T_{ramp} = 10 °C/min.



(a) (b)

Figure S2 (a). Top view of Bi_2Te_3 film deposited onto a TiN substrate (500 °C); (**b**)**.** Cross sectional SEM of Bi_2Te_3 film deposited on SiO_2 substrate (500 °C)

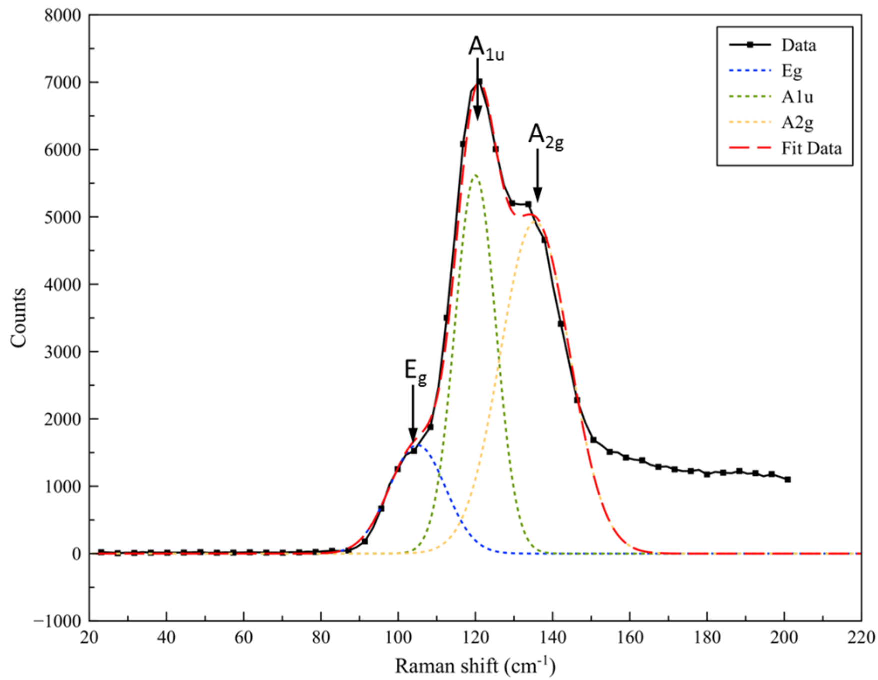


Figure S3. Raman spectrum of Bi_2Te_3 thin film formed by LPCVD from $[BiCl_3(Te^nBu_2)_3]$ (black trace) and simulated fit (red trace). The broad features to high frequency are from the SiO_2 substrate.

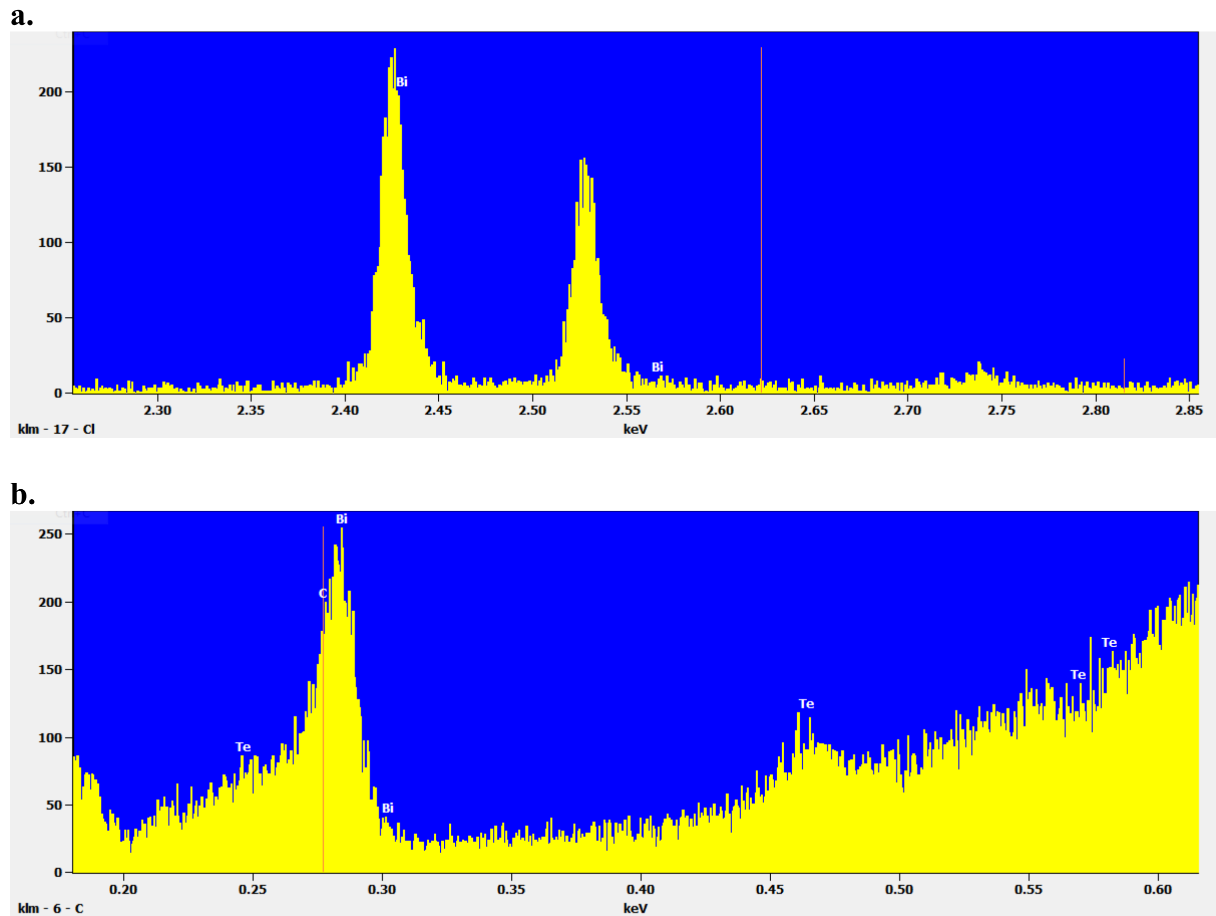


Figure S4. WDX spectra for a Bi_2Te_3 thin film over two energy windows. **a.** demonstrates the absence of a Cl Kα or Kβ peak (at the energies shown by the red lines), **b.** shows the overlapping C Kα and Bi N6-N5 peaks.

Table S1: Lattice parameters for Bi_2Te_3 samples, refined from x-ray diffraction data against a literature pattern (ref. 19) using the PDXL programme.

Sample (see Fig. 4)	a	c
a. 100 µm well	*	30.40(2)
b. SiO_2 substrate	4.378(10)	30.46(5)
c. TiN substrate	4.3885(14)	30.444(13)
d. Literature (ref. 19)	4.3849	30.4971

* the a lattice parameter could not be refined from this data as only 0 0 l peaks were observed

Microfocus and pole figure XRD analysis of microscale Bi_2Te_3 arrays

9 data sets were collected with a 50 micron beam centred on wells of different sizes (100 µm (regions 1,2,3), 60 µm (regions 4,5,6) and 40 µm (regions 7,8,9) as indicated in Figure S6a). Data are dominated by 0 0 *l* reflections with *l* = 6, 15, 18 and 21 showing a high degree of *c*-axis orientation. The data sets are very similar (Figure S6b), except that overall peak intensities are clearly grouped into 3 different values based on the well size (Figure S6b inset).

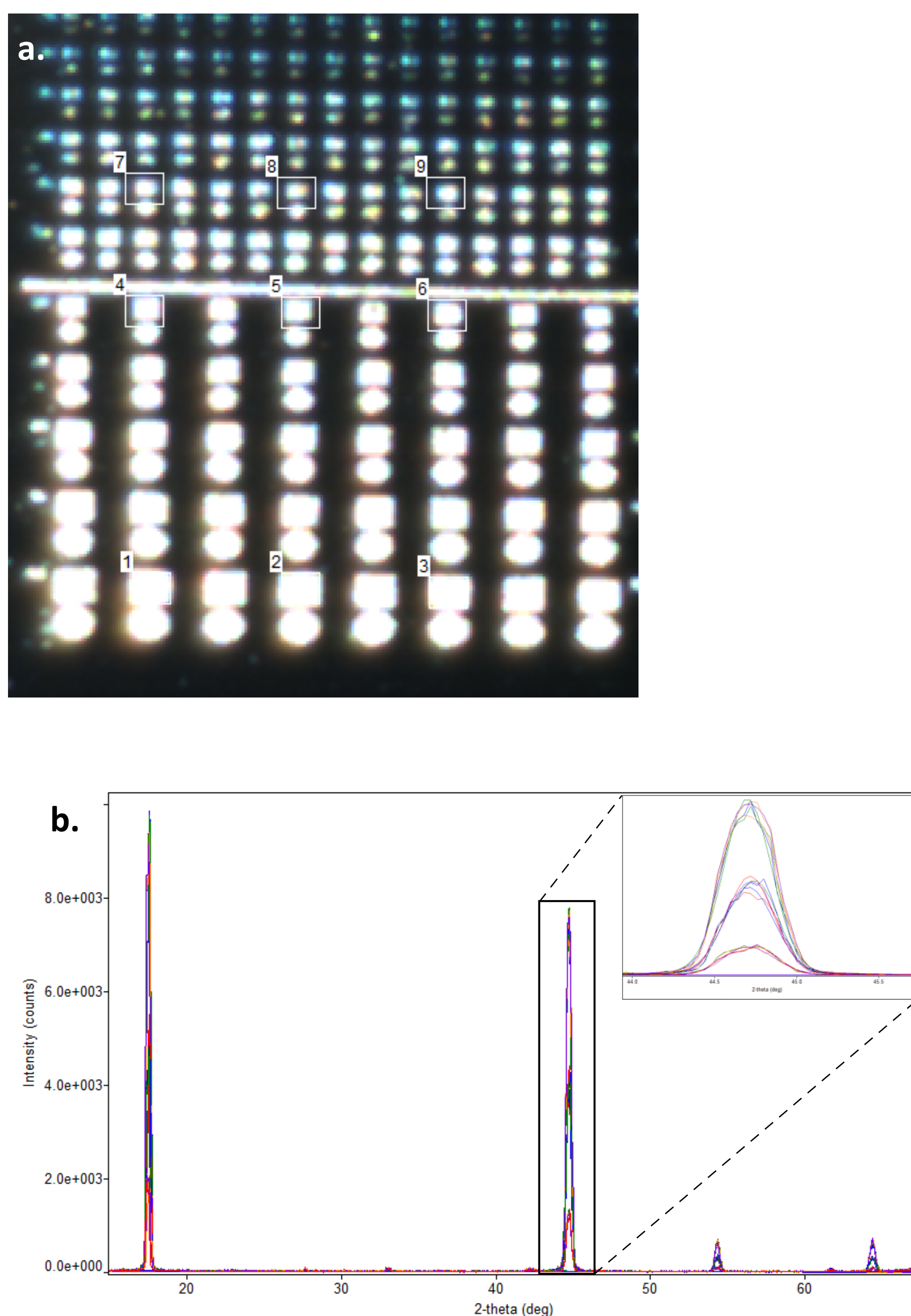


Figure S5. a. Optical microscope view of Bi_2Te_3 array, with areas of beam for microfocus X-ray scans highlighted. **b.** Overlaid patterns from 9 different wells in Bi_2Te_3 array. Insert shows zoomed in 0 0 15 peak. In each case data plus fit line are shown.

Equation S1. Pole figure analysis. Calculation of inclination of the diffraction vector to measure the 0 1 5 reflection if <0 0 1> is inclined at the surface normal with α_{001} = 90°:

$$\alpha_{015} = 90 - \tan^{-1}\left(\frac{c/5}{a\cos 30}\right)$$

$a = 4.4$

$c = 30.4$

Therefore $\alpha_{015} = 32.1°$