Substrate preparation: Sputtered SiO$_2$ and TiN substrates and photolithographically patterned TiN/SiO$_2$ substrates were prepared as described previously. 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$_2$Te$_3$: XRD measurements were carried out using a Rigaku Smartlab diffractometer with a 9 kW Cu-K$_\alpha$ 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$_2$Te$_3$ 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, N₂-purged glove box. The temperature was increased at a rate of 10 °C/min. TGA of [BiCl₃(TeⁿBu₂)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 Bi₂Te₃ being the final residue (theoretical residual mass = 38%). The TGA also indicates limited reagent evaporation occurs at ambient pressure.

![Figure S1. TGA plot for [BiCl₃(TeⁿBu₂)₃] collected under Ar with T_ramp = 10 °C/min.](image-url)
Figure S2 (a). Top view of Bi$_2$Te$_3$ film deposited onto a TiN substrate (500 °C); (b). Cross sectional SEM of Bi$_2$Te$_3$ film deposited on SiO$_2$ substrate (500 °C).

Figure S3. Raman spectrum of Bi$_2$Te$_3$ thin film formed by LPCVD from [BiCl$_3$(Te$^n$Bu$_2$)$_3$] (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$_2$Te$_3$ 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$_2$Te$_3$ samples, refined from x-ray diffraction data against a literature pattern (ref. 19) using the PDXL programme.

<table>
<thead>
<tr>
<th>Sample (see Fig. 4)</th>
<th>a</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. 100 μm well</td>
<td>*</td>
<td>30.40(2)</td>
</tr>
<tr>
<td>b. SiO$_2$ substrate</td>
<td>4.378(10)</td>
<td>30.46(5)</td>
</tr>
<tr>
<td>c. TiN substrate</td>
<td>4.3885(14)</td>
<td>30.444(13)</td>
</tr>
<tr>
<td>d. Literature (ref. 19)</td>
<td>4.3849</td>
<td>30.4971</td>
</tr>
</tbody>
</table>

* the a lattice parameter could not be refined from this data as only 0 0 1 peaks were observed
Microfocus and pole figure XRD analysis of microscale Bi$_2$Te$_3$ 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$_2$Te$_3$ array, with areas of beam for microfocus X-ray scans highlighted. b. Overlaid patterns from 9 different wells in Bi$_2$Te$_3$ 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 \( \alpha_{001} = 90^\circ \):

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

\( a = 4.4 \)

\( c = 30.4 \)

Therefore \( \alpha_{015} = 32.1^\circ \)