

Protrusions, Depressions, and Indentation Hardness of Pressure-Gradient-Sputtered $(\text{Bi}_2\text{Te}_3)_x(\text{Sb}_2\text{Te}_3)_{1-x}$ Thin Films

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Supplementary Materials

Table S1. Depressions in the stylus profiles of the thinnest film at each composition. The film segment is the 1.0 mm section from 1.0 to 2.0 mm of each profile; the bare segment is the substrate on the other side of the film edge. A depression is counted where the profile falls more than 0.1 μm below the mean line, and its width is taken at half its depth. Masked values exclude a 20 μm window around each film depression.

Quantity	$x = 0.00$	0.24	0.48	0.73	1.00
Film: depressions (number)	9	1	—	3	5
Film: deepest (nm)	320	189	—	406	855
Film: width at half depth (μm)	4.7–11.3	4.0	—	4.7–8.0	4.0–8.0
Film: masked P_q (nm)	21.5	4.8	—	16.5	12.3
Film: masked P_{sk}	+0.23	−2.01	—	−1.83	−3.13

Quantity	$x = 0.00$	0.24	0.48	0.73	1.00
Bare: segment length (mm)	0.55	0.53	0.52	0.53	0.63
Bare: depressions (number)	0	1	4	0	8
Bare: deepest (nm)	40	434	1149	64	2059
Bare: width at half depth (μm)	—	6.0	4.7–7.3	—	3.3–9.3

At $x = 0.48$, the film profile is dominated by peaks, the highest reaching $4.2 \mu\text{m}$ above the bare-substrate level (Figure S3c), so the minima between them, down to approximately $0.9 \mu\text{m}$ below the plateau, are not counted as depressions. A bare substrate from the same lot, profiled over 0.35 mm (526 points), gives $P_q = 1.9 \text{ nm}$, $P_{sk} = -0.59$, and $P_{ku} = 2.7$, with a peak-to-valley height of 9.2 nm . The depressions in the bare segments are polishing defects of the alumina; they are $3.3\text{--}9.3 \mu\text{m}$ wide at half depth, a similar range to that of the film depressions ($4.0\text{--}11.3 \mu\text{m}$). The number of troughs crossed varies strongly between plates, from zero to eight. At $x = 1.00$, two film depressions reach below the level of the bare substrate (Figure 3c of the main text).

Table S2. Dates and calibration constants of the indentation tests. Here C_f is the frame compliance, recorded with each data set and subtracted from the raw displacement, and A/A_{ideal} is the ratio of the calibrated contact area to the ideal Berkovich area, $23.96h_c^2$, at a contact depth h_c of 25 nm . The target depth was set between 8% and 12% of the film thickness.

x	Date of test	Calibration state	C_f (nm mN ⁻¹)	A/A_{ideal}	Target depth (nm)
0.00	2 Nov 2023	1	0.313	2.0	87
0.24	18 Jul 2025	2	0.281	2.7	57
0.73	18 Jul 2025	2	0.281	2.7	48
1.00	17 Oct 2024	1	0.313	2.0	63

Each calibration state covers one Sb-rich and one Bi-rich film. The hard–soft division of the main text therefore holds within each state: $x = 0.00$ against $x = 1.00$ under state 1, and $x = 0.24$ against $x = 0.73$, tested on the same day, under state 2. The compliance correction, $C_f F_{\text{max}}$, is 0.03–0.12 nm at the maximum loads of 0.10–0.37 mN, below 0.2% of the depth. The films at $x = 0.24$ and 0.73 were tested in one session, so a thermal drift common to the session adds the same displacement to both films during the 5 s hold. For these two films, the hold displacements, 4.7 and 11.3 nm on average, differ significantly ($p < 0.001$, Welch’s t -test). The contact area A was obtained from the contact depth h_c with the area function $A = 23.96h_c^2 + C_1h_c + C_2h_c^{1/2} + \dots + C_8h_c^{1/128}$, calibrated on fused silica ($E = 73$ GPa, $\nu = 0.17$). The coefficients are $C_1 = 606.5$, $C_2 = -12.4$, and $C_4 = -15.77$ for state 1, with the others zero, and $C_1 = 1508.7$, $C_2 = -8954.4$, $C_3 = 5764.0$, $C_4 = 6317.3$, $C_5 = 4117.6$, $C_6 = 2311.4$, $C_7 = 1220.5$, and $C_8 = 626.6$ for state 2 (A in nm², h_c in nm). At $h_c = 50$ nm, A/A_{ideal} is 1.5 for state 1 and 1.8 for state 2. The indenter modulus and Poisson’s ratio were 1140 GPa and 0.07. Loading and unloading were linear at approximately 0.1 mN s⁻¹ (load steps of 2 μ N every 20 ms), and the 5 s hold was sampled every 25 ms (200 samples in each film). A correction for creep during unloading after Feng and Ngan (ref. [70] of the main text), $1/S_e = 1/S + \dot{h}/|\dot{F}|$,

with the creep rate $\dot{h}$ over the last 1 s of the hold and the unloading rate $\dot{F} = 0.1 \text{ mN s}^{-1}$, gives $H_{IT} = 1.81, 1.91, 0.81$, and 1.03 GPa and $E_{IT} = 55.5, 70.3, 41.2$, and 44.0 GPa at $x = 0.00, 0.24, 0.73$, and 1.00 , respectively.

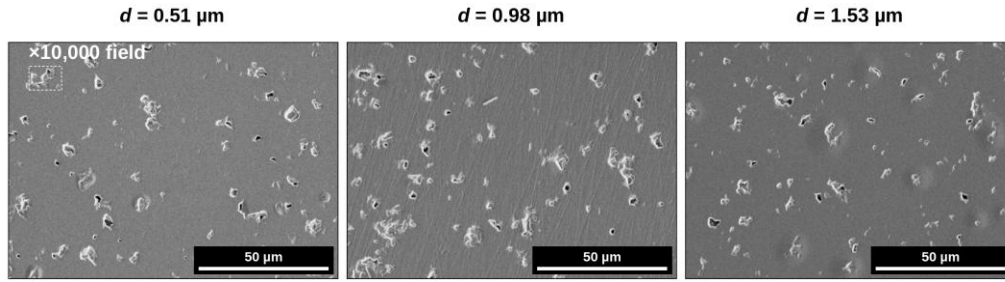


Figure S1. Dark features in $\times 1000$ FE-SEM images of the $x = 1.00$ films, $0.51, 0.98$, and $1.53 \mu\text{m}$ thick. The dashed rectangle on the first image marks the field of view of a $\times 10,000$ image. The image of the $0.51 \mu\text{m}$ film is reproduced as Figure 3b of the main text.

Thresholding at the mean intensity minus two standard deviations, with only connected regions larger than 20 pixels kept, gives mean equivalent diameters of $1.07, 1.03$, and $1.01 \mu\text{m}$. The areal fractions are $0.27\%, 0.25\%$, and 0.19% , and the number density is $(2.4\text{--}3.0) \times 10^{-3} \mu\text{m}^{-2}$. The largest feature measures $2.2 \mu\text{m}$. For thresholds from 1.5 to 2.5 standard deviations below the mean intensity, the three films keep the same order in diameter and areal fraction.

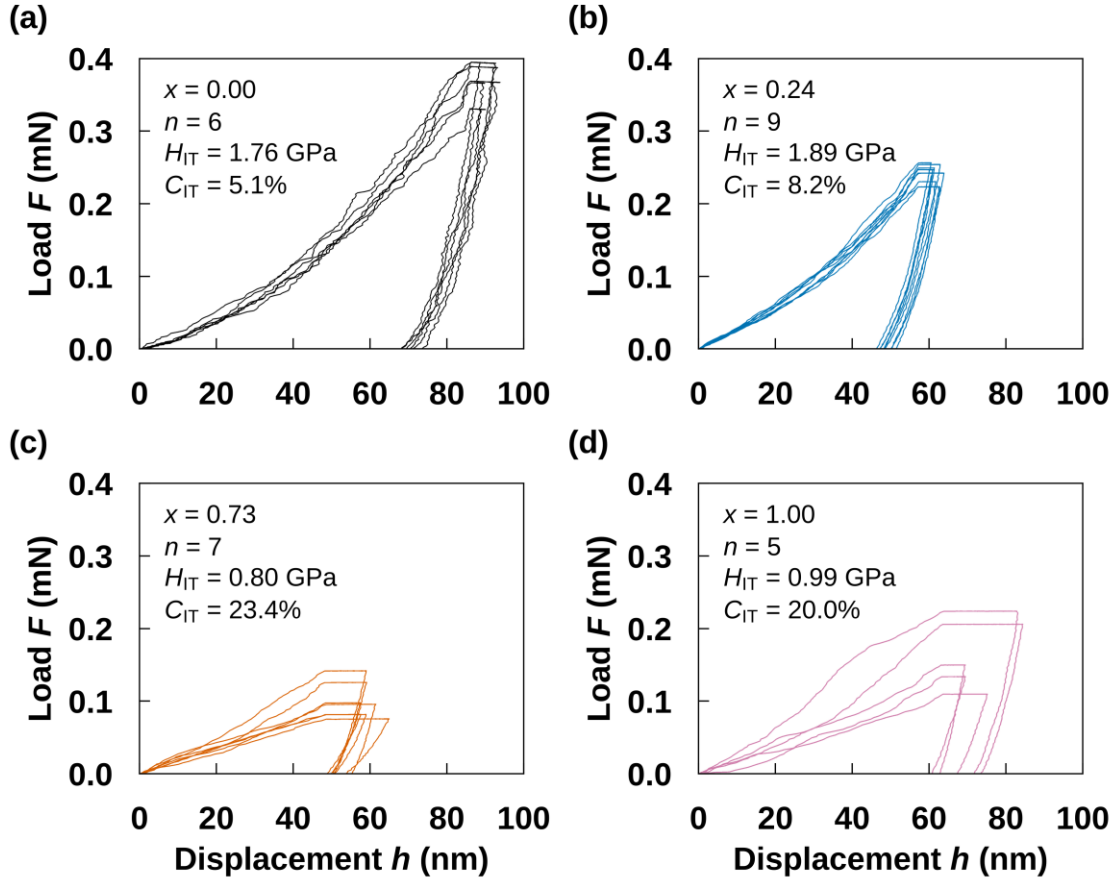


Figure S2. Indentation load–displacement curves: (a) $x = 0.00$, (b) $x = 0.24$, (c) $x = 0.73$, and (d) $x = 1.00$. Every indent is plotted, with the approach segment before contact removed. The horizontal segment at maximum load is the 5 s hold.

During the hold, the penetration advances by 4.4 and 4.7 nm on average at $x = 0.00$ and 0.24, and by 11.3 and 12.7 nm at $x = 0.73$ and 1.00. The hard–soft division is therefore visible in the raw curves, independent of the Oliver–Pharr analysis.

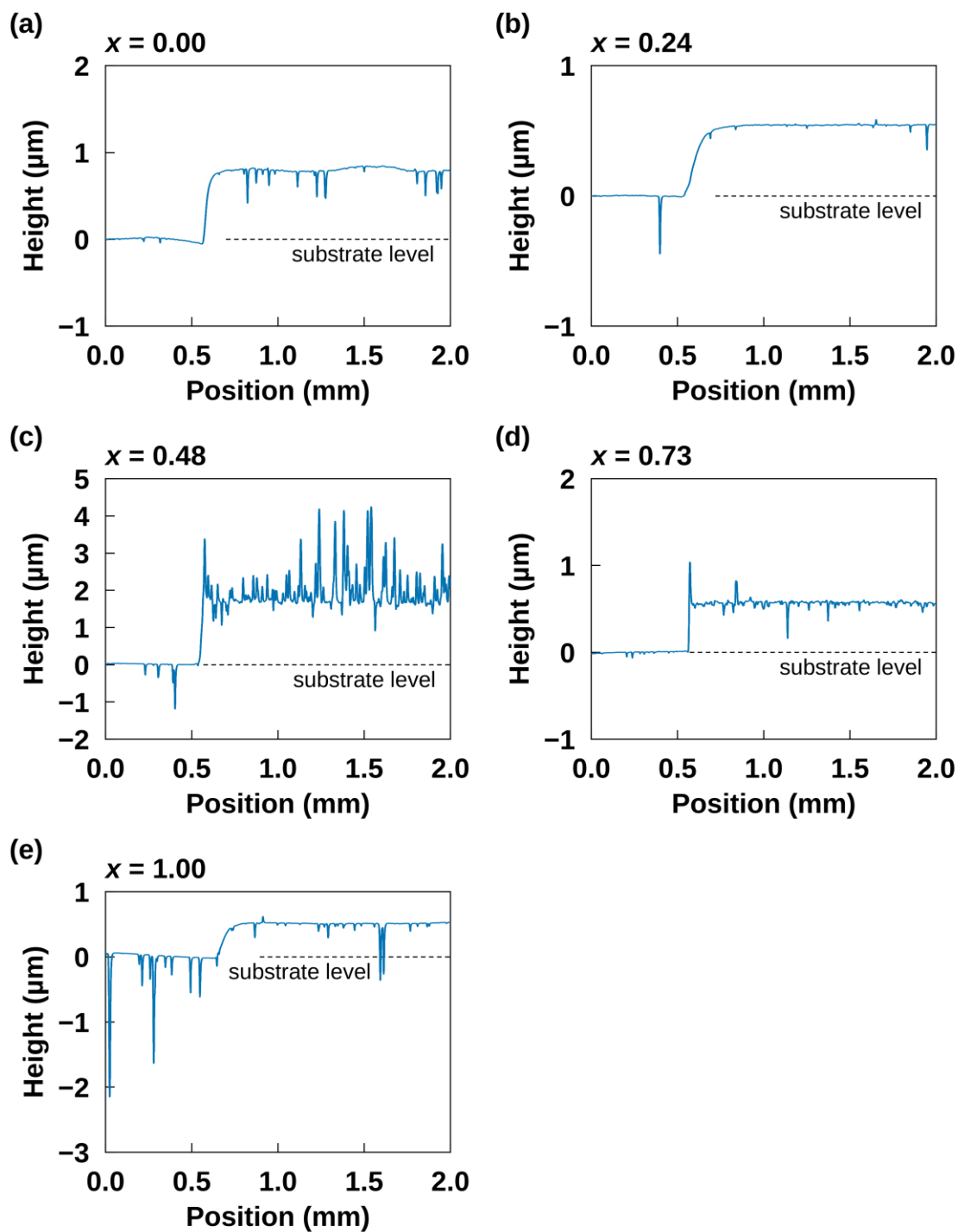


Figure S3. Stylus profiles across the film edge of the thinnest film at each composition: (a) $x = 0.00$, (b) $x = 0.24$, (c) $x = 0.48$, (d) $x = 0.73$, and (e) $x = 1.00$. Both sides of the edge were

leveled with a common slope. The depressions on the bare substrate are polishing defects.

The dashed line marks the level of the bare substrate, extended under the film.

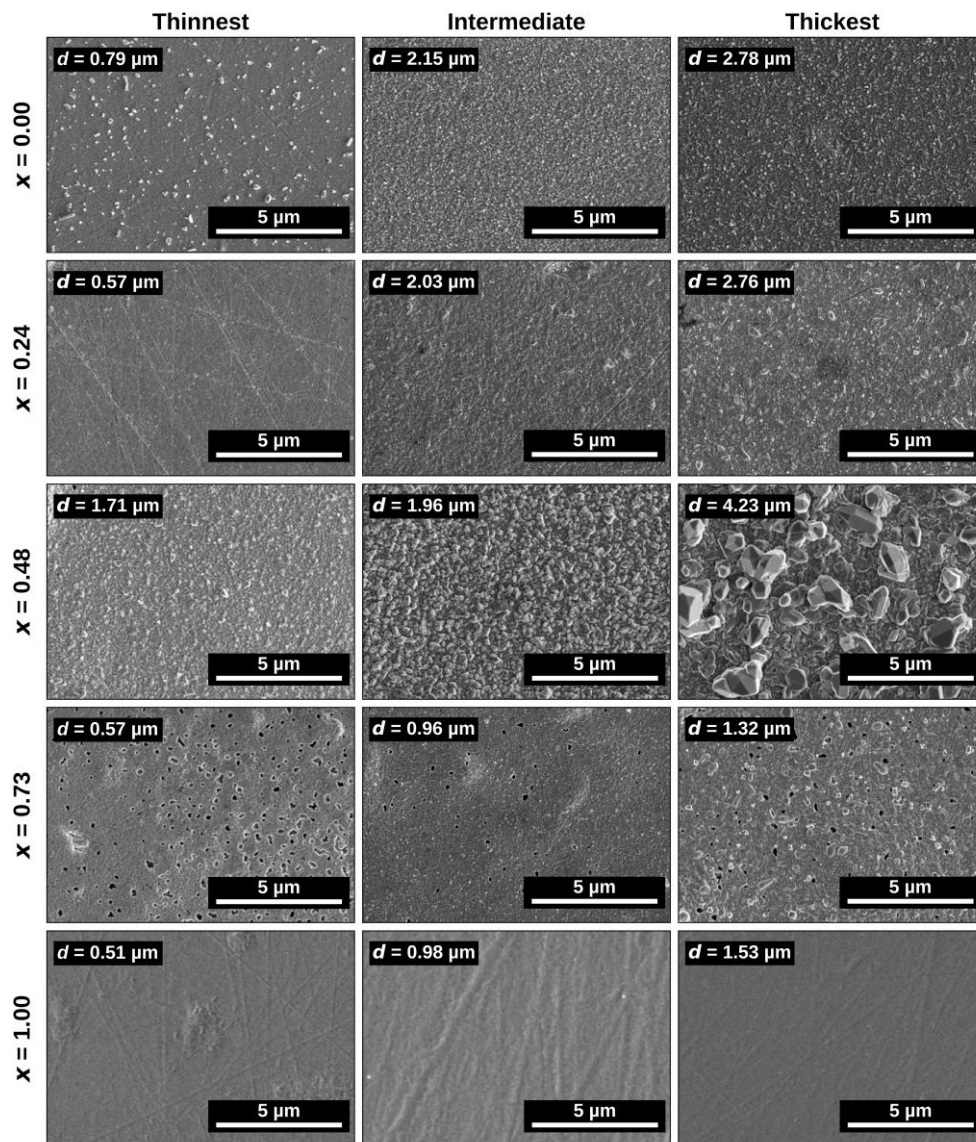


Figure S4. FE-SEM images ($\times 10,000$) of all 15 $(\text{Bi}_2\text{Te}_3)_x(\text{Sb}_2\text{Te}_3)_{1-x}$ films. Rows: composition x ; columns: the thinnest, intermediate, and thickest film of each composition

(Table 1 of the main text). The thickness d is marked on each image. The thinnest and thickest films at $x = 0.24$, 0.48 , and 1.00 are reproduced in Figure 3a of the main text.

At nearly equal thickness, 1.96 , 2.03 , and $2.15\ \mu\text{m}$, the film at $x = 0.48$ consists of faceted grains $0.2\text{--}0.5\ \mu\text{m}$ across separated by dark gaps, the film at $x = 0.24$ of closely packed grains $0.1\text{--}0.3\ \mu\text{m}$ across, and the film at $x = 0.00$ of still finer grains. These three films grew at the usual rates of their targets (10.9 , 11.3 , and $11.2\ \text{nm min}^{-1}$). At $x = 0.48$, the grains stand above the surface at all three thicknesses (1.71 , 1.96 , and $4.23\ \mu\text{m}$) and coarsen into faceted crystals up to approximately $2\ \mu\text{m}$ across at $4.23\ \mu\text{m}$. The films at $x = 0.00$ ($0.79\text{--}2.78\ \mu\text{m}$) and $x = 0.24$ ($0.57\text{--}2.76\ \mu\text{m}$) show no grains larger than $0.5\ \mu\text{m}$; the $0.79\ \mu\text{m}$ film at $x = 0.00$ carries discrete particles $0.1\text{--}0.4\ \mu\text{m}$ across on a smooth matrix. At $x = 0.73$, the films show pits below $1\ \mu\text{m}$ across, and the $1.32\ \mu\text{m}$ film also shows faceted grains $0.2\text{--}0.5\ \mu\text{m}$ across. No film at $x = 0.73$ or 1.00 reaches $2\ \mu\text{m}$. The films at $x = 1.00$ ($0.51\text{--}1.53\ \mu\text{m}$) show faint lines and streaks. At equal thickness, the coarse faceted grains distinguish $x = 0.48$ from $x = 0.00$ and 0.24 .

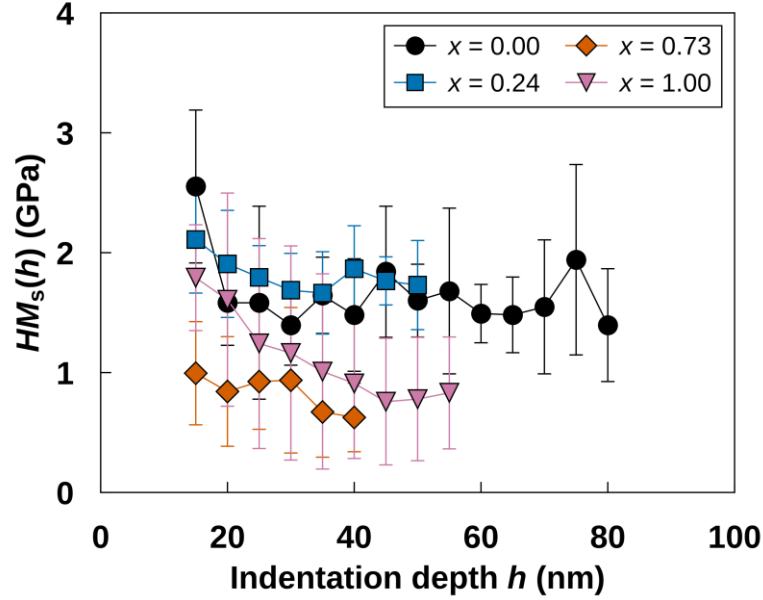


Figure S5. Depth dependence of the Martens hardness, $HM_s(h)$, obtained from the loading curves of Figure S2. For each indent, h was fitted against $F^{1/2}$ in a 10 nm window moved along the loading segment in 5 nm steps, and $HM_s = 1/(26.43 \text{ m}^2)$ was evaluated from the slope m according to ISO 14577-1. Symbols are the means over the indents of each film ($n = 5\text{--}9$), error bars are one standard deviation, and the last point of each film lies at least 5 nm below the depth at which the hold began.

The fit over 50–90% of the maximum load reproduces the HM_s values of Figure 4a of the main text. From 25 nm to the maximum depth, $HM_s(h)$ stays at 1.4–1.9 GPa for the Sb-rich films. For the Bi-rich films, it falls from 0.9–1.3 GPa at 25 nm to 0.6–0.9 GPa at 40–55 nm and does not rise toward the substrate. At equal depths from 25 nm, the mean $HM_s(h)$ of each Bi-rich film lies below that of both Sb-rich films. Below 25 nm, the calibrated contact area exceeds the ideal Berkovich area by more than a factor of 2 (Table S2), and the films are not

compared there. Because $HM_s(h)$ depends only on the slope of h against $F^{1/2}$, it is independent of the zero point of the depth and of the contact-area function.