Supplementary Material

Defect Passivation by Annealing Enables Stable Transport in Li-Doped Mg_2Sn Epitaxial Films for Microfabricated Thermoelectric Devices

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1. Experimental Methods

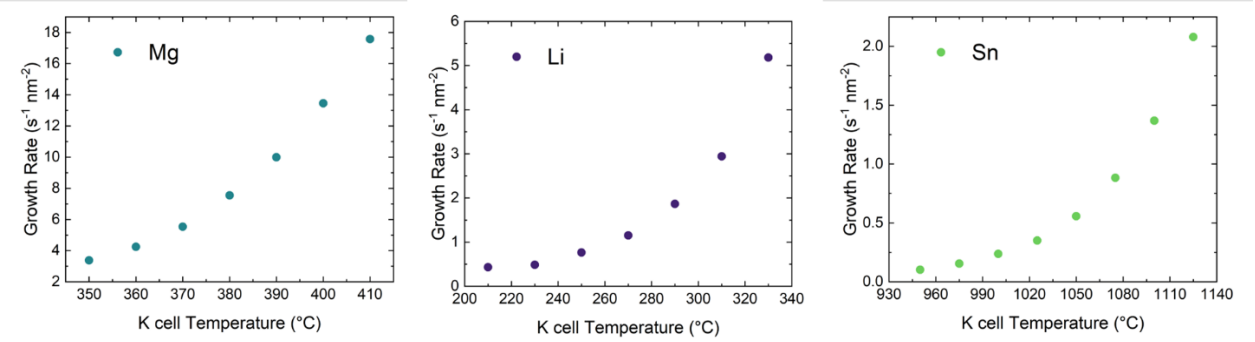

Figure S1. Growth Rate of K-cell for Mg, Li, and Sn

Table 1. List of samples $Mg_{2-x}Li_xSn$ for measurement along with their synthesis conditions. The Sn rate was fixed at 1.60 $s^{-1}nm^{-2}$ for all samples.

Nominal Composition	Mg K-Cell T (°C)	Mg Rate ($s^{-1}nm^{-2}$)	Li K-Cell T (°C)	Li Rate ($s^{-1}nm^{-2}$)	Sn K-Cell T (°C)	Sn Rate ($s^{-1}nm^{-2}$)
Mg_2Sn	405	15.0	0	0	1100	1.60
$Mg_{1.95}Li_{0.05}Sn$	402.9	14.63	210	0.375	1100	1.60
$Mg_{1.92}Li_{0.08}Sn$	402.9	14.63	210	0.375	1100	1.60
$Mg_{1.90}Li_{0.10}Sn$	402	14,25	249.8	0.75	1100	1.60

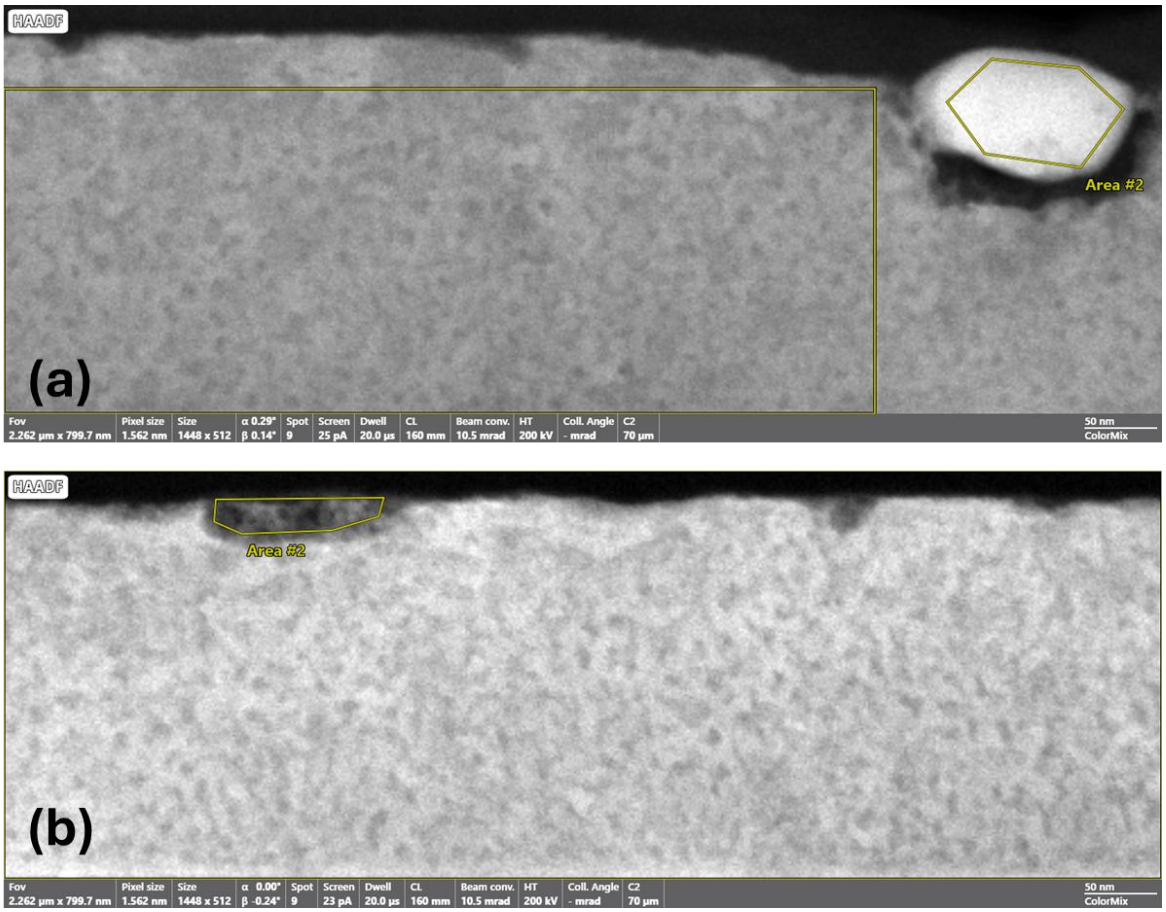

Fig. S2 Cross-sectional STEM–HAADF images of the nominal 5% Li film used for TEM–EDS quantification (Table S2): (a) as-deposited (as-grown) state and (b) after annealing. The outlined regions indicate the EDS acquisition areas, where Area #1 corresponds to the Mg_2Sn matrix region (selected away from the film/substrate interface) and Area #2 corresponds to a surface secondary-phase region associated with Sn-rich features. Scale bars: 50 nm.

Table S2. Cross-sectional TEM–EDS atomic fractions (at%) and associated errors for the nominal 5% Li film in the as-deposited (as-grown) and annealed states. Area #1 corresponds to the Mg_2Sn matrix region selected away from the film/substrate interface; Area #2 corresponds to a surface secondary phase region. The Mg/Sn (atomic) ratio is calculated from the Mg and Sn atomic fractions for each area and condition. Li is not reported because it is not reliably quantified by EDS.

Condition	Area	Element	Atomic fraction (at%)	Atomic error (at%)	Mg/Sn ratio (atomic)
As-grown	#1 Mg_2Sn matrix region	Mg	57.13	5.26	**1.88**
		Sn	30.39	4.18	
		O	12.48	1.49	
	#2 surface secondary phase region	Mg	3.50	0.82	-
		Sn	76.52	2.12	
		O	19.98	1.76	
Annealed	#1 Mg_2Sn matrix region	Mg	54.40	5.25	**1.89**
		Sn	28.77	3.85	
		O	16.83	1.91	
	#2 surface secondary phase region	Mg	40.20	4.92	-
		Sn	12.96	1.65	
		O	46.84	3.93	

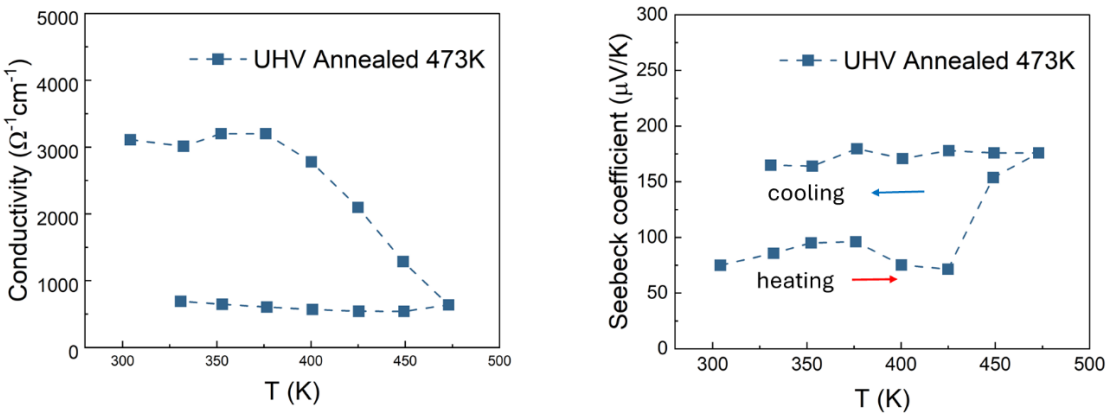

Fig. S3. Cyclic heating–cooling measurements of electrical conductivity (left) and Seebeck coefficient (right) for $Mg_{2-x}Li_xSn$ (x = 0.05) films after 473 K annealing under UHV inside MBE chamber. The UHV-annealed sample shows transport behavior similar to the as-grown state, in contrast to the stabilization observed after low-vacuum annealing.

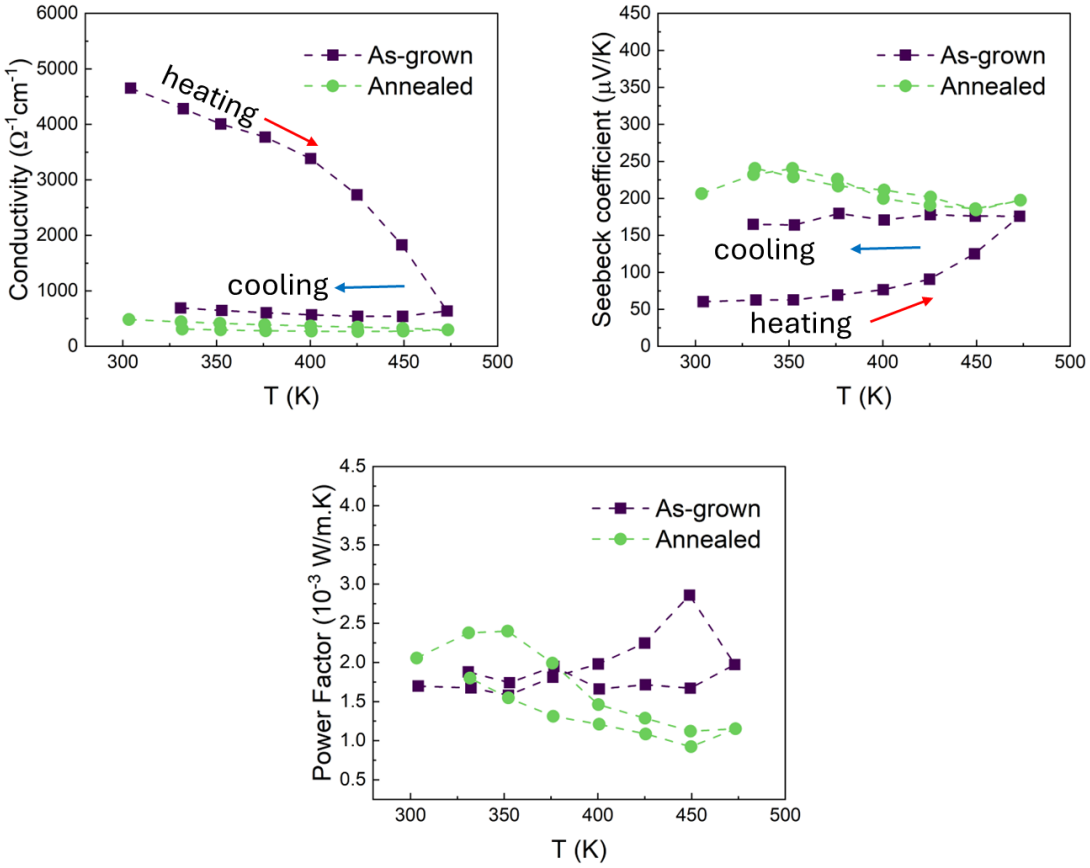

Fig. S4 cyclic heating–cooling TE properties measurement tests for as-grown and annealed $Mg_{2-x}Li_xSn$ (x = 0.05).

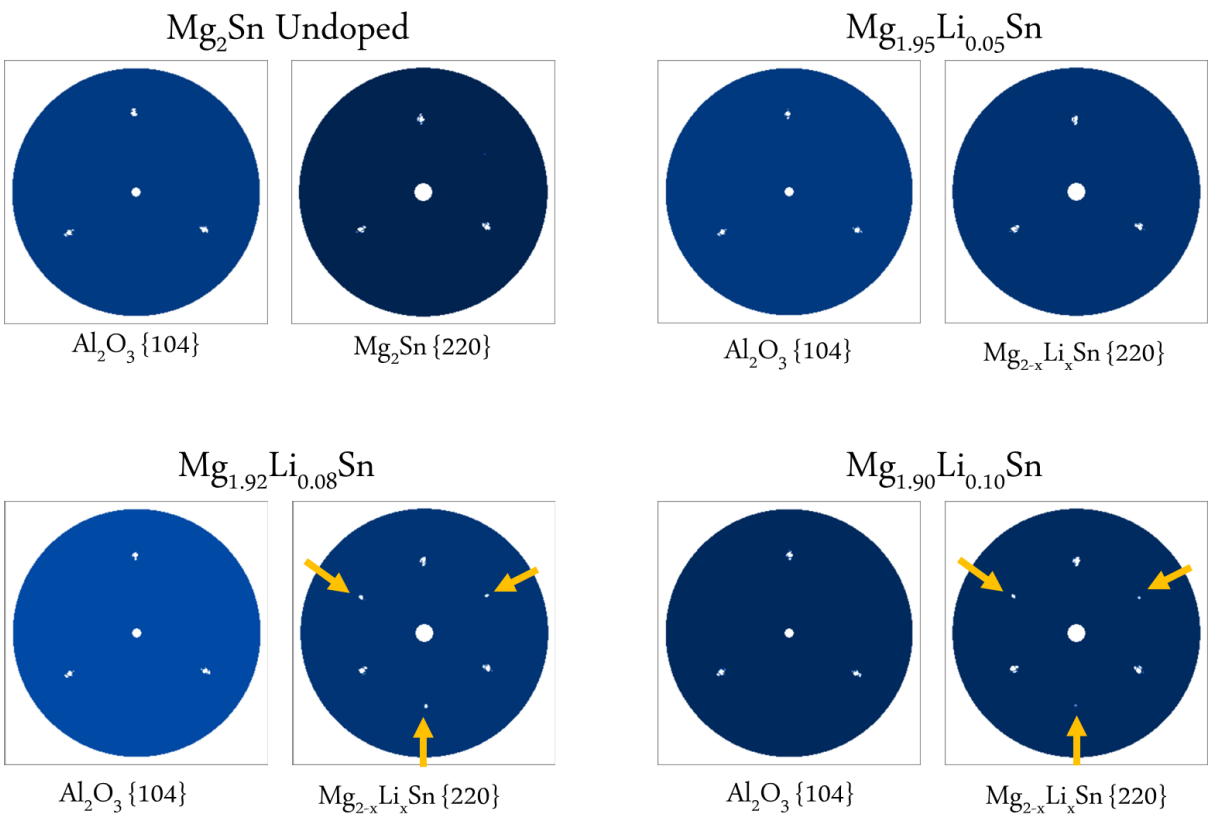

Fig. S5 X-ray pole figure of the as-grown nominally Mg_xLi_xSn films grown on sapphire(0001). The threefold symmetry of the main poles confirms the epitaxial relationship $(111)_{Mg_2Sn} \parallel (0001)_{Al_2O_3}$ and $[11\bar{2}]_{Mg_2Sn} \parallel [10\bar{1}0]_{Al_2O_3}$ with a fixed in-plane alignment. Minor additional spots that appear at higher nominal Li contents (indicated by yellow arrows) suggests a small amount of stacking faults in the (111) epitaxial film.