

Electronic Supplementary Information (ESI)

Anomalous Thermoelectricity of Pure ZnO from 3D Continuous Ultrathin Nanoshell Structures

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SUPPORTING FIGURES AND CAPTIONS

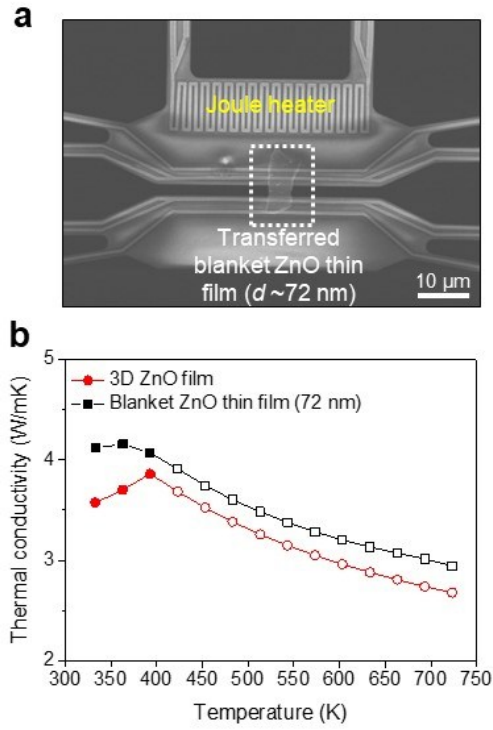


Fig. S1 Measurement of the thermal conductivity (κ) of a blanket ZnO thin film with a thickness of 72 nm. (a) SEM image of a transferred blanket ZnO thin film with a thickness of 72 nm to a microfabricated thermoelectric measurement platform (MTMP). (b) Measurement and estimation κ of a blanket ZnO thin film compared to that of a 3D ZnO film as a function of temperature.

SUPPORTING TABLES AND CAPTIONS

Process	Temperature (°C)	ALD cycles (n)	DEZ pulse (sec)	Ar purge (sec)	H ₂ O pulse (sec)	Ar purge (sec)
Blanket ZnO film (3.2 μm)	150	12,000	1	15	1.5	15
Protecting ZnO layer on 3D templates (9 nm)	90	60	1	15	1.5	15
Additional ZnO layer on 3D templates (27 nm)	150	240	1	15	1.5	15
Additional ZnO layer on 3D templates (63 nm)	150	480	1	15	1.5	15
Additional ZnO layer on 3D templates (99 nm)	150	720	1	15	1.5	15

Table S1 Information of ALD processes for depositing ZnO layers with different thicknesses on a bare-sapphire substrate and 3D epoxy templates.

Preparation method	Product form	Power factor near RT (mW/mK ²)	Peak Power factor (mW/mK ²)	κ near RT (W/mK)	Lowest κ (W/mK)	zT near RT	Peak zT
Pressing & sintering ¹	Bulk (15 mm thick)	0.00306 @ 300 K	-1.5 @ 1273K	-49 @ 300 K	-5 @ 1273K	0.000062588 @ 300 K	-0.02 @ 1000 K
Spark plasma sintering ²	Bulk (12 mm thick)	0.00077 @ 300 K	-0.036 @ 1200K	-15.5 @ 473 K	-7 @ 1200K	-0.00002256 @ 473 K	0.2 @ 1173 K
Pressing & sintering ³	Bulk (10 mm thick)	0.02256 @ 350 K	0.1 @ 1000K	33 @ 350K	-3 @ 1000K	0.000239 @ 350 K	-0.02 @ 1000 K
Theoretical simulation ⁴	Thin film (5376 atoms)	NA	0.2-0.3 @ 600K	NA	1.3 @ 303 K	NA	0.2 @ 600 K
ALD ⁵	Thin film (100 nm thick)	NA	NA	1.9 @ 303 K	NA	NA	NA
ALD ⁶	Thin film (130 nm thick)	-0.3 @ 300 K	0.576 @ 705K	NA	NA	NA	NA
ALD ⁷	Thin film (130 nm thick)	0.14 @ 300 K	NA	NA	NA	NA	NA
ALD ⁸	Superlattice thin film (100 nm film-thick)	0.018 @ 300 K	NA	NA	NA	NA	NA
Sputtering ⁹	Thin film (250 nm thick)	0.0001 @ 325 K	0.0002 @ 500K	NA	NA	NA	NA
Sol-gel process ¹⁰	Thin film (unknown thickness)	-0.00196 @ 320 K	0.00239 @ 470K	NA	NA	NA	NA
ALD (This Work)	Thick film (3.2 μ m thick)	0.188 @ 333 K	0.302 @ 693 K	135.48 @ 333 K	72.86 @ 723 K	0.00047 @ 333 K	0.0029 @ 723 K
ALD (This Work)	3D Nanostructured thick film (72 nm shell-thick, 10 μ m film-thick)	0.183 @ 333 K	0.292 @ 693K	3.57 @ 333 K	2.74 @ 693 K	0.0172 @ 333 K	0.072 @ 693 K

Table S2 Comparison of the thermoelectric performance achieved by this work with previously reported results using pure ZnO.¹⁻¹⁰

	3D ZnO	Blanket ZnO (3.2 μm)	Blanket ZnO (72 nm)
κ (W/mK)	3.6	135.5	4.1
σ (S/m)	3740	2960	6300
zT	0.0172	~ 0.0005	~ 0.02

Table S3. Measured thermoelectric properties of 3D ZnO, Blanket ZnO (3.2 μm) and Blanket ZnO (72 nm) at 333K

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