Supplementary Information

Thermoelectric Performance of PbSe Quantum Dot Films

Dajiang Yang[1,*,ξ,**], Chenguang Lu[2,*, ξ], Huiming Yin[1] and Irving P. Herman[2]

[1] *Department of Civil Engineering and Engineering Mechanics, Columbia University, New York, NY 10027.*

[2] *Department of Applied Physics and Applied Mathematics, Columbia University, New York, NY 10027.*

1. Materials

The raw materials for the preparation of PbSe QDs were: lead acetate trihydrate white powder ($Pb(CH_3COOH)_2.3H_2O$), 99.99% Sigma Aldrich, Squalane ($C_{30}H_{62}$), 99.99% Aldrich, and oleic acid ($CH_3(CH_2)_7CH$, and pills of selenium (Se), trioctylphosphine (TOP) solution, metalchalcogenide SnS_2 and hydrazine (N_2H_4, 99.99% Aldrich).

2. $(N_2H_5)_4Sn_2S_6$ MCC preparation

All preparations were performed in a nitrogen-filled glove box.

Elemental sulfur was first dissolved in N_2H_4 to yield a 1M S-N_2H_4 solution. 118.7 mg elemental tin (1 mmol) was dissolved in a mixture of 3 mL 1M S-N_2H_4 solution and 1 mL N_2H_4

* Corresponding Authors: e-mail: *dajiangyang@gmail.com*, *cl2551@columbia.edu*

ξ These authors contributed equally

** Dr. Yang is currently with OmniVision Technologies, Inc. Santa Clara, CA 95054.

upon stirring at room temperature. In the alternative procedure noted in the main text, these samples were prepared by dissolving 183 mg (1 mmol) SnS_2 in a mixture of 1 mL of 1M S-N_2H_4 solution and 3 mL N_2H_4. Both methods gave a slightly yellow clear solution and the concentration of $(N_2H_5)_4Sn_2S_6$ was nominally 0.25 mol/L.

3. Seebeck Coefficient

Cr/Au thin metal lines were used for the thermometer in the Seebeck coefficient measurements; the four-probe resistance change with the temperature of the typical metal lines is shown in Figure S1. The localized temperature can be determined from the calibration curve by measuring the four probe resistances of the metal lines. The change of the thermal power factor, $S^2\sigma$, with temperature is plotted in Figure S2, using the data presented in Figures 3(b) and 5. Normally this temperature dependence follows the same trends as the Seebeck coefficient. There is no clear size dependence observed here.

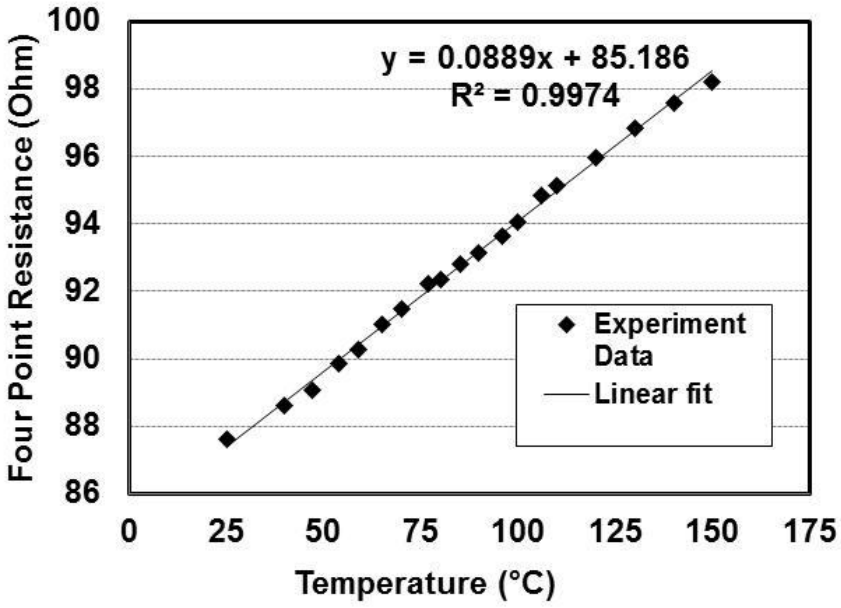


Figure S1. Measuring temperature from resistances, for the Seebeck coefficient measurements.

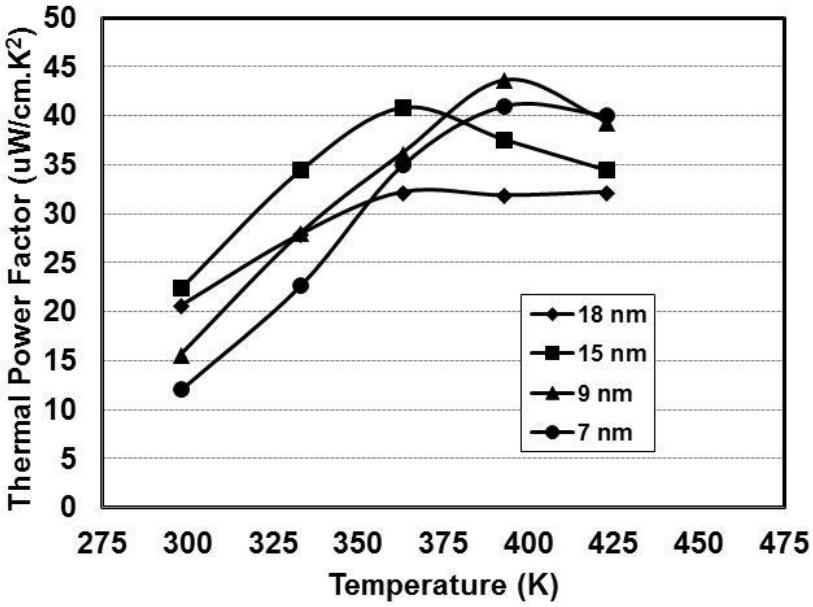


Figure S2. Thermal power factors of the PbSe(SnS_2) QD films.

4. Thermal conductivity

The thermal conductivity measurements were performed in vacuum. An embedded heater and temperature controller were used to control the sample temperature. A Gwinstek frequency synthesizer was used to produce sine waves from 10-1000 Hz and a lock-in amplifier (Princeton Applied Research 128A) was used to extract the 3ω signal V_3 from the outputs of a precision differential amplifier (Analog devices AD624).

The 3ω method was modified for measuring thermal properties of thin films deposited on a Si substrate.[1, 2] The thermal conductivity of the QD films was determined by:

$$K_f = \frac{P d_f}{2b\{\Delta T_{s+f}(\omega) - \Delta T_s(\omega)\}} \qquad \text{(S1)}$$

where $\Delta T_{s+f}(\omega)$ and $\Delta T_s(\omega)$ are the temperature oscillations from the substrate with and without thin film, P, b and d_f are the power per unit length of the heater, half width of the heater and

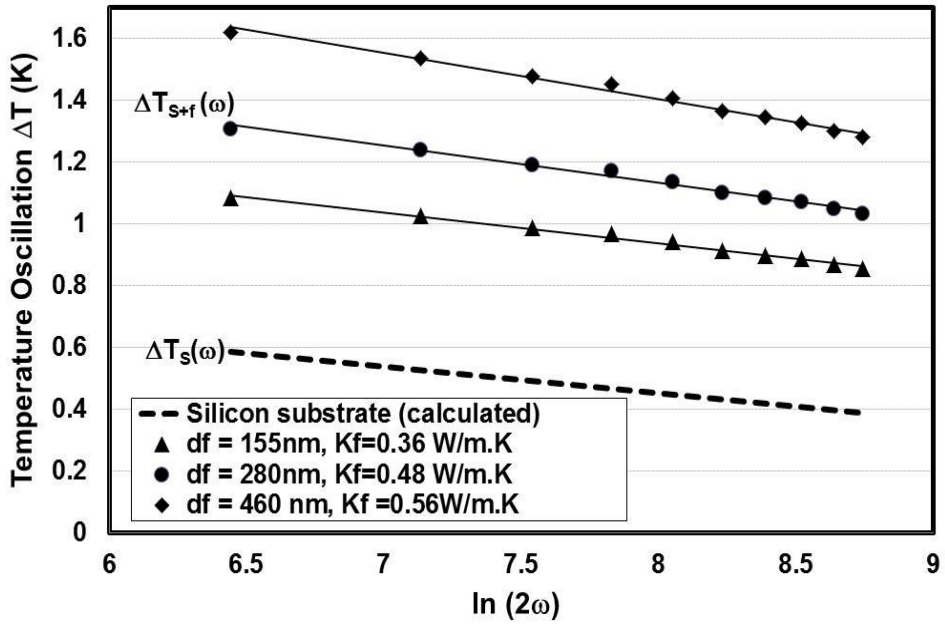
thickness of the QD films, respectively. The $\Delta T_s(\omega)$ was calculated from the third harmonic voltage drop across the metal line, $V_{3\omega}$,

$$\Delta T(\omega) = \frac{2V_{3\omega}}{\alpha V} \qquad \text{(S2)}$$

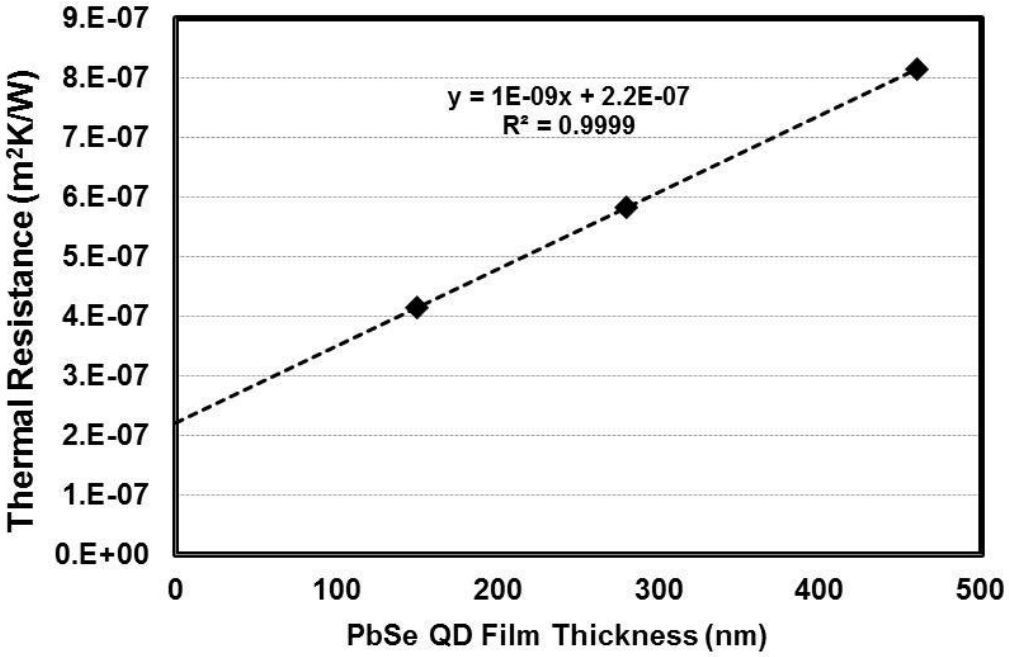
where α and V are the temperature coefficient of the resistance of the heater and the voltage drop across the metal line. All voltages are expressed as rms voltages. Figure S3(a) shows the temperature oscillation $\Delta T(\omega)$ as function of the modulation frequency from 10 to 1000 Hz at room temperature for 7 nm PbSe(SnS_2) QD films with thicknesses of 155 nm, 280 nm, and 460 nm coated on Si substrate and covered with 180 nm SiO_2. The effective thermal conductivity K_f was determined through Eq. (S1). The total effective thermal resistance of the films R_f can be expressed as:

$$R_f = \frac{d_f}{K_f} = R_c + R_{SiO2} + \frac{d_f}{K_i} \qquad \text{(S3)}$$

where, R_c, R_{SiO2} and K_i are the total contact thermal resistance, thermal resistance of the SiO_2 and the intrinsic thermal conductivity of the QD film. Figure S3(b) shows the effective thermal resistance as a function of the QD film thickness. By extrapolating the thermal resistance to zero film thickness, we get the thermal resistance of $R_c + R_{SiO2}$ of approximately 2.22×10^{-7} m^2K/W, which is within the range of other reported values.[1, 3] The intrinsic thermal conductivity K_i of the PbSe(SnS_2) QD films can be inversely determined from Eq. (S3). The K_i of films of 9 nm, 15 nm and 18 nm QDs were determined following the same procedure.



(a)

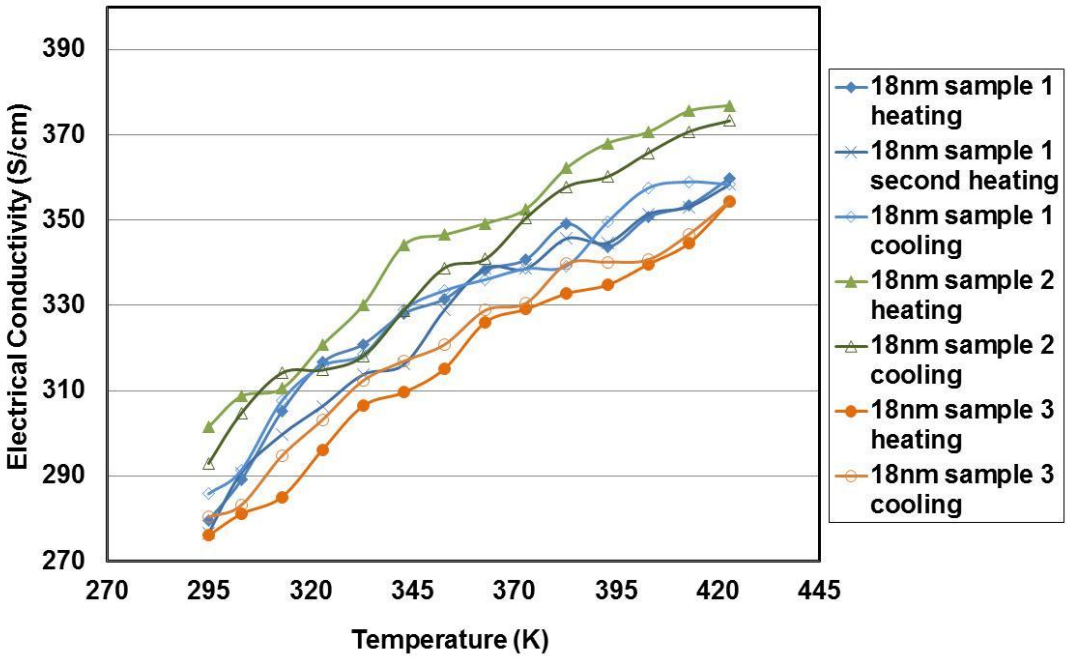


(b)

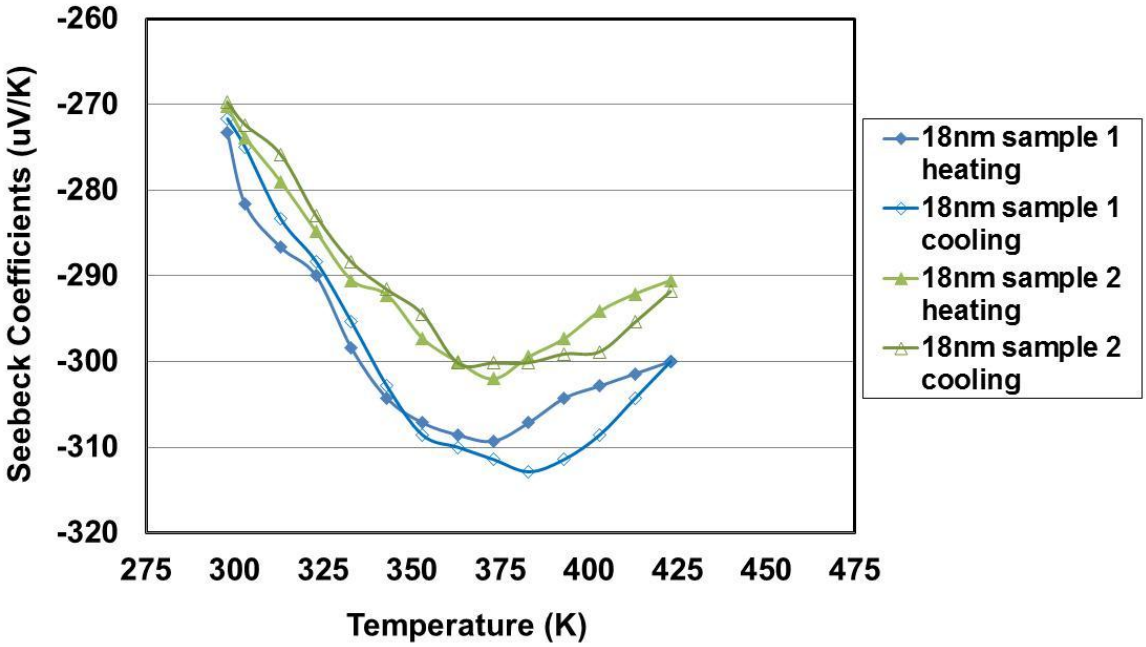
Figure S3. (a) Temperature oscillations during thermal conductivity measurements, and (b) thermal resistance determined for the difference thickness PbSe(SnS_2) QD films.

5. Data Repeatability

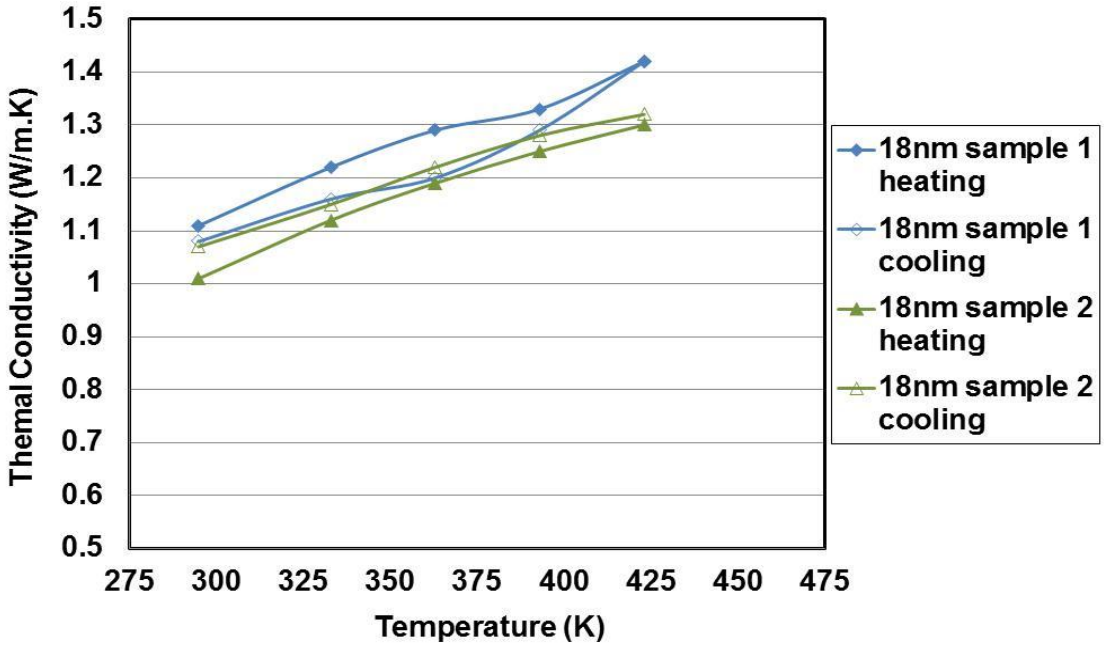
To verify the repeatability of the temperature dependence of the data and test for potential hysteresis and modification of the films during heating, the electrical conductivity, Seebeck coefficient, and thermal conductivity of the 18 nm PbSe(SnS_2) QD films were recorded during both heating and cooling ramps, as shown in Figure S4. Typically, the data were consistent after temperature cycling.



(a)



(b)



(c)

Figure S4. Measurements of the PbSe(SnS_2) QD film (a) electrical conductivity, (b) Seebeck coefficient, and (c) thermal conductivity during cycles of increasing *T* (heating) and subsequent

decreasing *T* (cooling). For one electrical conductivity measurement this was followed by another heating cycle.

References

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