Supporting Information

Zr vacancy interface: an effective strategy for collaborative optimization of ZrNiSn-Based thermoelectric performance

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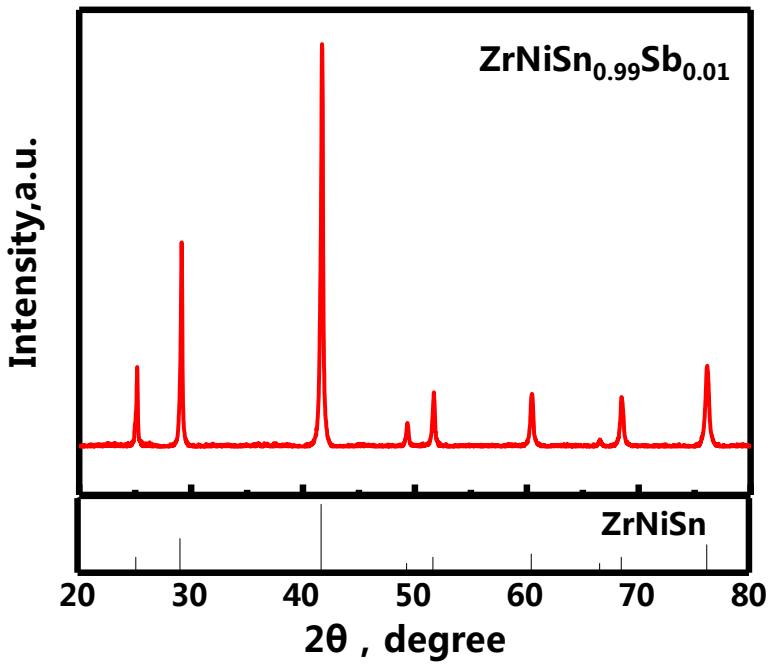


Fig S1. XRD pattern of the as-prepared $ZrNiSn_{0.99}Sb_{0.01}$ (ZNSS) powders.

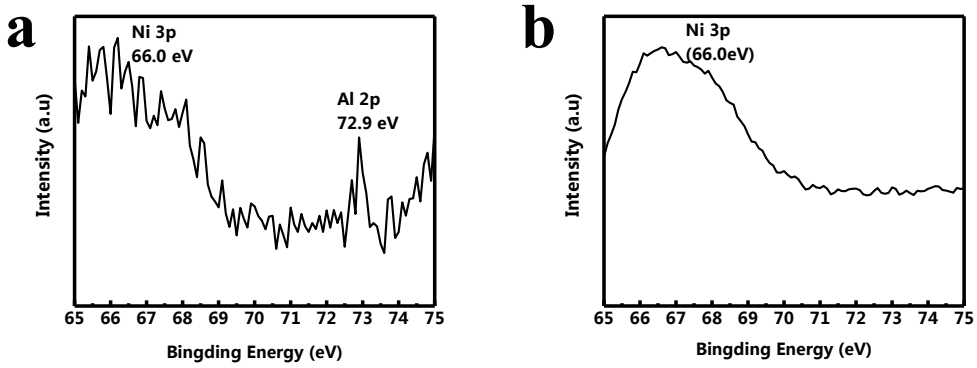


Fig S2. (a) XPS spectra for the as-prepared ZNSS with ultra-thin Al_2O_3 interface layer and (b) the sintered ALD coated ZNSS sample.

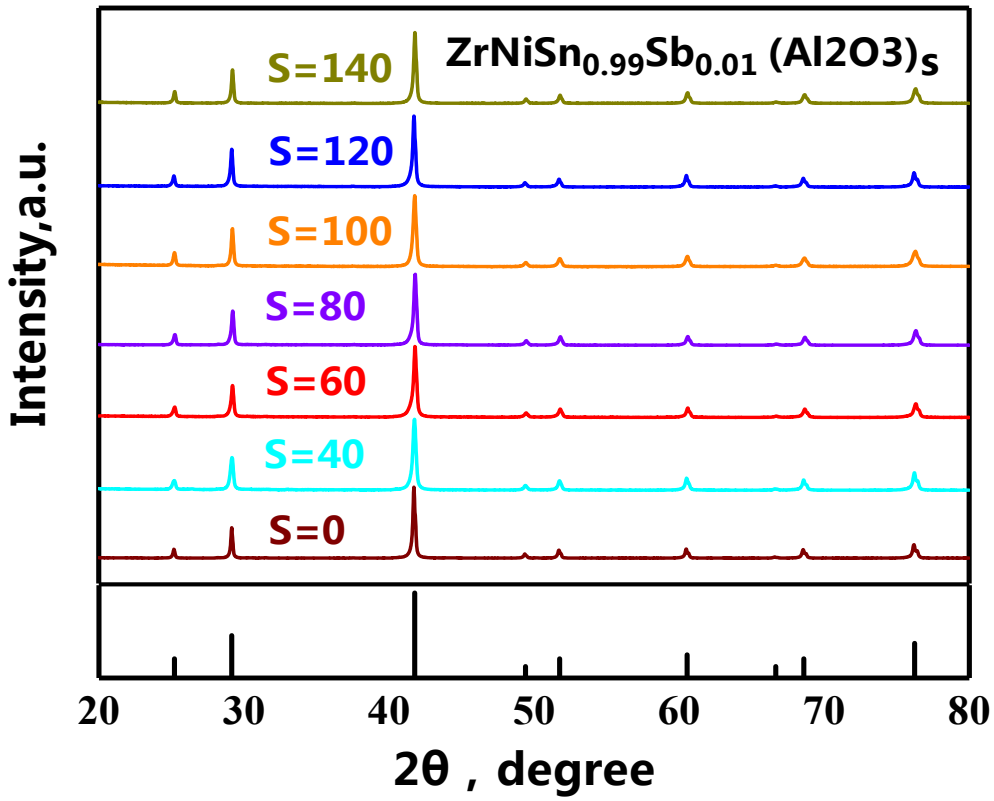
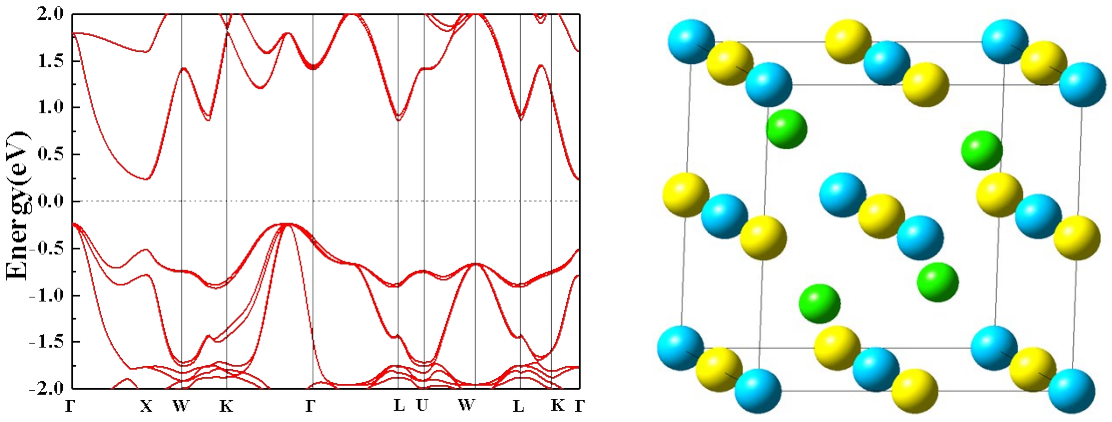
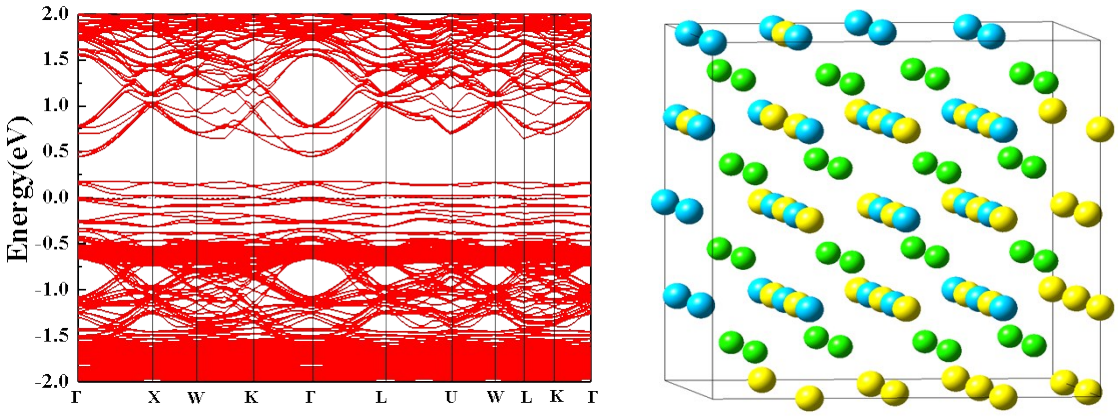


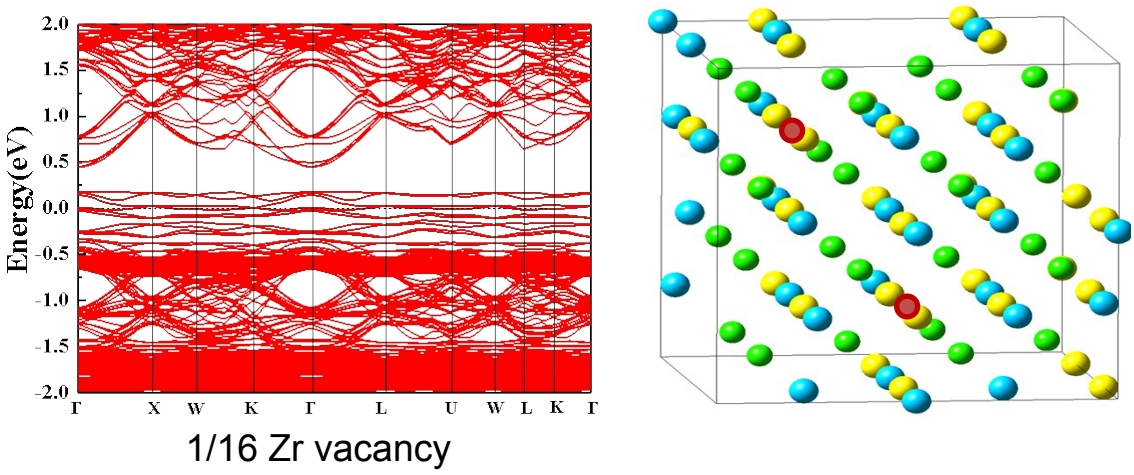
Fig S3. XRD pattern of the samples with different ALD cycles after SPS process.



pristine



1/32 Zr vacancy



1/16 Zr vacancy

Fig S4. Schematic diagram and band structure diagram of ZrNiSn and different Zr vacancies. The impurity level is located at the position of the blue dotted line in Fig. b and c.

$Zr_{(1-x)}NiSn$	bottom of conduction band	energy barrier
x=0	0.236 ev	0 ev
x=1/32	0.411 ev	0.175 ev
x=1/16	0.447 ev	0.211 ev

Table S1. The position of the bottom of conduction band of different Zr vacancies and the interface barrier between energy band of different Zr vacancies and matrix ZNSS

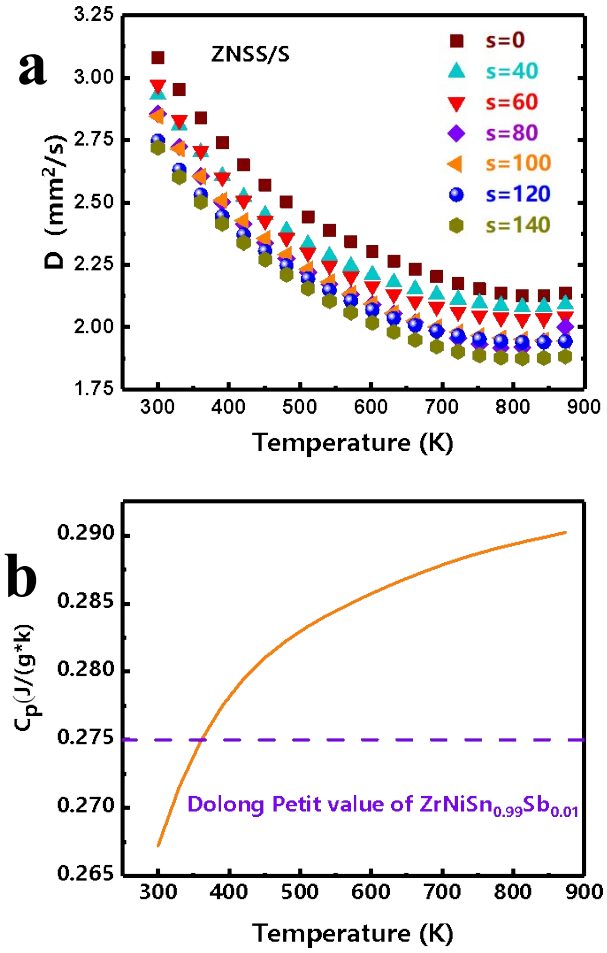


Fig S5. (a) Temperature dependence of Thermal diffusion coefficient (D) with different ALD cycles. (b) Temperature dependent specific heat capacity Cp for ZNSS.

These *m** values were used to plot Pisarenko lines that demonstrate carrier concentration dependence of the Seebeck coefficient in degenerate semiconductors via the following equation:

$$S = \frac{8\pi^2 k_B^2 T}{3eh^2} m_d^* \left(\frac{\pi}{3n}\right)^{2/3} \quad (1)$$

where m^*_d is the density of states (DOS) effective mass, and k_B, e, and h are the Boltzmann constant, elementary charge, and the Planck constant, respectively. By utilizing the S and n values at room temperature, the m^*_d was determined and compared with literature data.

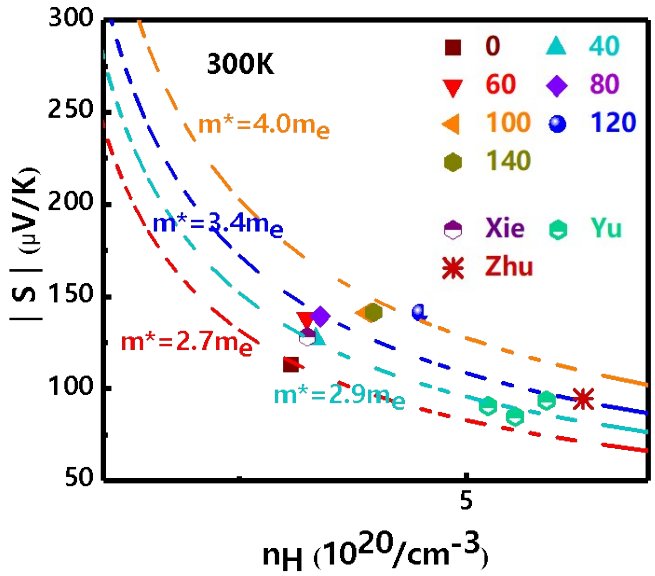


Fig. S6 Carrier-concentration- dependent Seebeck coefficient (S).

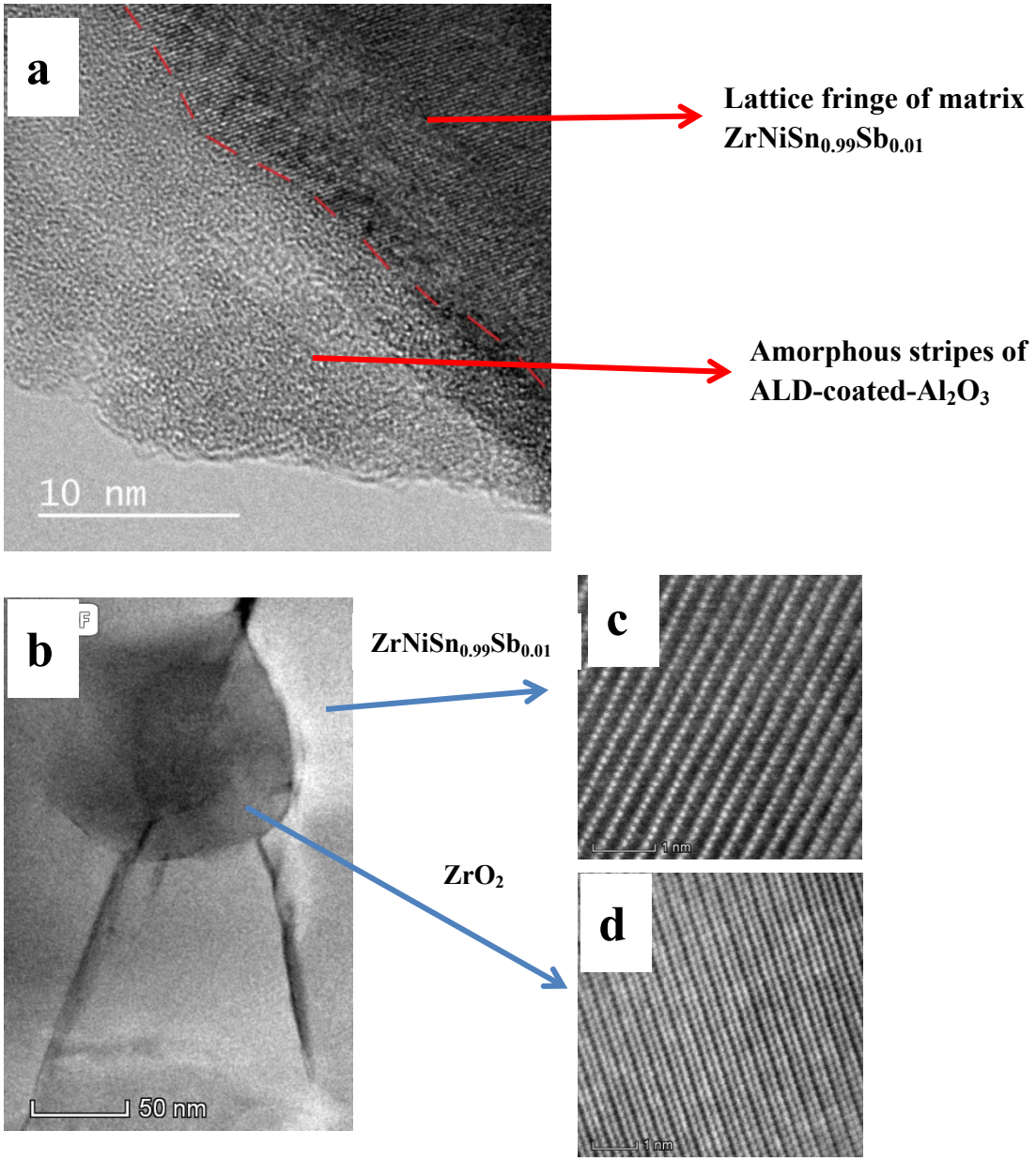


Fig. S7 (a) HRTEM images at the ZnO/BTS interface of pre-sintered powder. (b)Low magnification TEM image, (c) (d) HRTEM images at the ZrO_2/ZNSS interface of sintered sample