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Supporting information for article:

Effect of growth modes on electrical and thermal transport of thermoelectric ZnO:Al films

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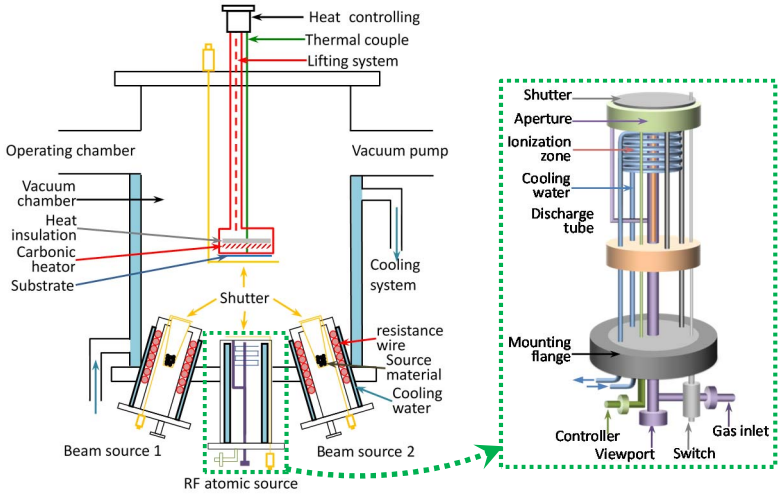

Fig. S1 Schematic diagram of vacuum thermal evaporation assisted by RF atomic source

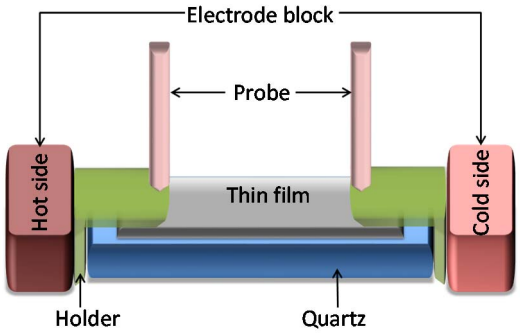

Fig. S2 Schematic diagram of sample holder for the resistivity and Seebeck coefficient measurement in the ZEM-3 equipment (Liu et al, 2018).

Table S1 Hall voltages of ZnO:Al films with the constant magnetic field of 0.558 T

Substrate temperature	AC(mV)	-AC(mV)	BD(mV)	-BD(mV)	Average
RT	1.0387	-0.9997	1.0353	-1.0032	1.019
300°C	1.5378	-1.4829	1.5155	-1.5001	1.509
450°C	9.1944	-9.1399	9.1943	-9.1431	9.168
600°C	21.5566	-21.2852	21.4698	-21.3792	21.423

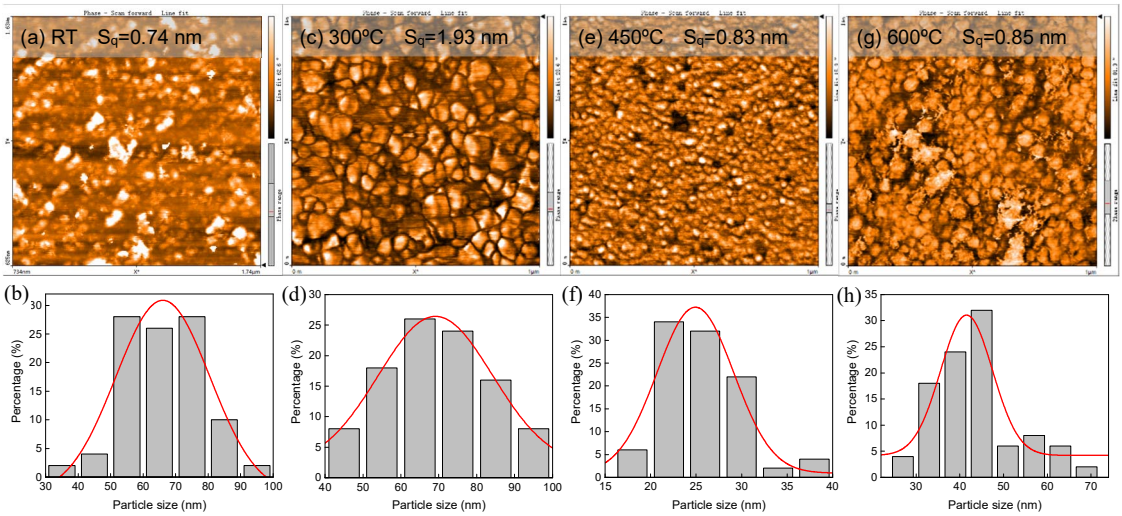

Fig.S3 AFM phase-contrast images (upper half) and particle size distribution (lower half) of ZnO:Al films at different substrate temperatures

The protruding particle is sparse but larger (66±31.18 nm) on RT film with a smaller surface roughness (S_q=0.74 nm). Spherical-shape particles (69.5±28.47 nm) distribute uniform on 300°C film with a surface roughness of 1.93 nm. The surface roughness is 0.83 nm and 0.85 nm at the substrate temperature of 450°C and 600°C respectively. The particle size on 450°C film is smaller (24.85±8.51 nm) while the particle size on 600°C film is 41.55±27.53 nm.

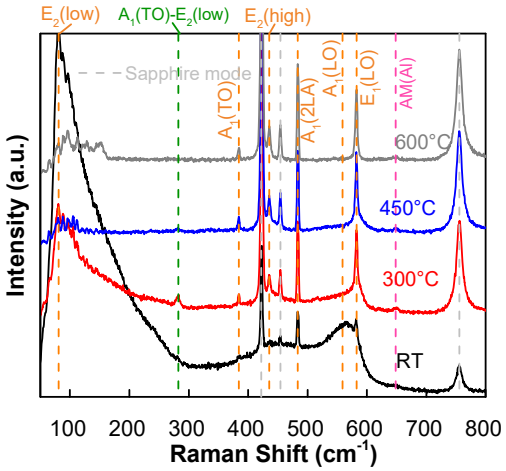

Fig.S4 Raman spectra of ZnO:Al films at different substrate temperatures

In the wurtzite ZnO structure, first-order vibration of the optic modes obeys the existence $\Gamma_{opt}=A_1+2B_1+E_1+2E_2$. Polar optical vibration in the lattice consists of transverse and longitude direction (A_1(TO) and A_1(LO)). Two-dimensional E_1mode split into transverse optical (TO) and longitudinal optical (LO) modes. The presence of E_2(low) mode associated

with the vibration of Zn atoms and E_2(high) mode of oxygen atoms in ZnO films. The peaks observed at 80 cm^{-1} ,435cm^{-1}correspond to the E_2(low) and the E_2(high) modes respectively. The transverse vibration of polar mode located at 384 cm^{-1} is the phonon confinement vibration induced by native defects of ZnO films which is resulted from oxygen vacancies. The acoustic vibration of ZnO films cause a shape A_1(2LA) peak at 483 cm^{-1}. The increase of micro-stress and carrier scattering can be achieved by vibration. Carrier mobility of ZnO:Al film shows the higher value at RT substrate temperature, the 600°C film exhibits the lower carrier mobility. The optical vibration of ZnO films at 560 cm^{-1} and 582 cm^{-1} attribute to vibration peaks of A_1(LO) and E_1(LO), caused by impurities and defects in ZnO:Al films. The anisotropy of ZnO:Al films can be also presented indirectly. A_1(LO) mode is parallel to the c-axis orientation and E_2(LO) mode is to the surface atom of substrate. Besides, the additional modes at 649 cm^{-1} is caused by Al dopant. The peak at 283 cm^{-1} on 300°C film attributes to the second-order [A_1(TO)-E_2(low)] vibration mode, caused by the unstable of polar and split vibration.

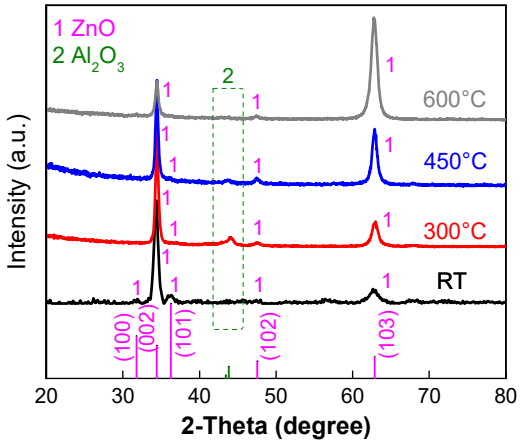

Fig.S5 XRD patterns of RF-assisted evaporated ZnO:Al films at different substrate temperatures.

An increase in substrate temperature results in the decrease of diffraction peak of ZnO (002) facet and gradual increase of (103) facet. The index M is to describe the texture coefficient of each planes:

$$\mathrm{M} = \frac{I_{(h_0k_0l_0)}/\sum I_{(hkl)}}{I_{0(h_0k_0l_0)}/\sum I_{0(hkl)}}$$

where I_0 is the standard XRD intensity and I is the experimental data. ∑ is the sum of the intensities of the peaks for (110), (002), (001), (102) and (103) planes. The direction with the highest intensity of the (002) facet on RT film is $M_{(002)}$=3.39. The index $M_{(002)}$ of ZnO:Al films

gradually decrease to 1.83, 1.38, 0.45 respectively with the substrate temperature increase to 300°C, 450°C and 600°C. Meanwhile, the index $M_{(103)}$ of (103) facet are 0.31, 0.47, 1.08 and 2.38 respectively as the substrate temperature increase from RT to 600°C.

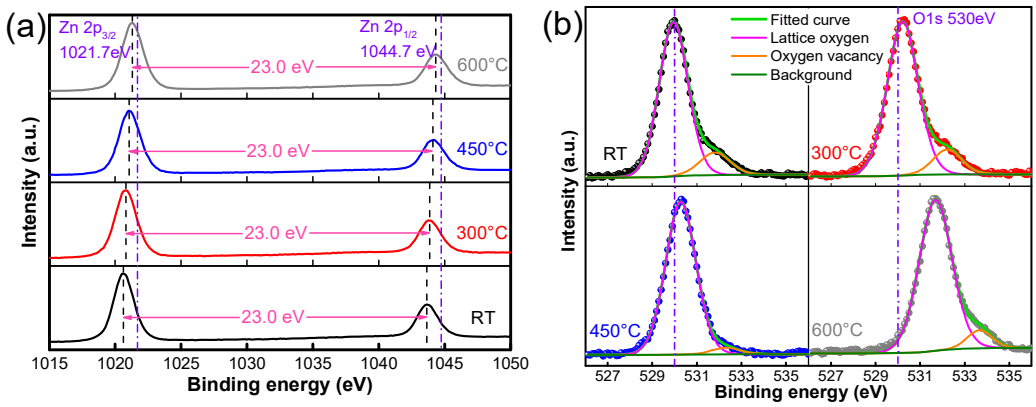

Fig. S6 High-resolution XPS spectra of O 1s (a) and Zn 2p (b) of ZnO:Al films at different substrate temperatures

High-resolution XPS spectra can be used to analyze the chemical states and native defects of ZnO:Al films. The Zn 2p spectra for the ZnO:Al films consist of two peaks, identified as Zn $2p_{3/2}$ and Zn $2p_{1/2}$. The binding energy difference of two peaks is 23.0 eV, as shown in Fig. S6(a). This chemical state of Zn is the same with ZnO. That is, the ZnO:Al film fabricated is the ZnO phase. The binding energy of O1s peak in ZnO:Al film at RT is 529.9 eV. The binding energy of Zn2p and O1s increases with the increase of substrate temperature. Furthermore, the O1s of ZnO:Al films are asymmetric peak which can be divided into two peaks of lattice oxygen and oxygen vacancies (V_O), as shown in Fig. S6(b). Content of V_O is expressed by the peak area. The concentrations of V_O are 13.48%, 13.00%, 3.76% and 8.25%, respectively at the substrate temperature of RT, 300°C, 450°C and 600°C.