# *In-situ* growth of high-performance (Ag, Sn) co-doped CoSb<sub>3</sub> thermoelectric thin films

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#### Abstract

Owing to the unique features, such as mechanically robust, low-toxic, high stability, and high thermoelectric performance, CoSb<sub>3</sub>-based skutterudite materials are among art-of-the state thermoelectric candidates. In this work, we develop a facile in-situ method for the growth of well-crystallinity (Ag, Sn) co-doped CoSb<sub>3</sub> thin films. This preparation method can efficiently control the dopant concentration and distribution in the thin films. Both the density functional theory calculation and the experimental results suggest that Sn and Ag dopants trend to enter the lattice and preferentially fill interstitial sites. Additionally, band structure calculation results suggest that the Fermi level moves into the conduction bands due to co-doping and eventually induces the increased electrical conductivity, which agrees with the optimization of carrier concentration. Moreover, an increase in the density of state after co-doping is responsible for the increased Seebeck coefficient. As a result, the power factors of (Ag, Sn) co-doped CoSb<sub>3</sub> thin films are greatly enhanced, and the maximum power factor achieves over 0.3 mW m<sup>-1</sup> K<sup>-2</sup> at 623 K, which is almost two times than that of the un-doped CoSb<sub>3</sub> film. Multiple microstructures, including Sb vacancies and Ag/Sn interstitial atoms as point defects, and a high density of lattice distortions coupled with nano-sized Ag-rich grains, lead to all scale phonon scatterings. As a result, a reduced thermal conductivity of ~0.28 W m<sup>-1</sup> K<sup>-1</sup> and a maximum ZT of ~0.52 at 623 K are obtained from (Ag, Sn) co-doped CoSb<sub>3</sub> thin films. This study indicates our facile in-situ growth can be used to develop high-performance dual doped CoSb<sub>3</sub> thins

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## 1. Introduction

Thermoelectric (TE) materials have widespread and significant application prospects in various fields of power generation and semiconductor cooling.[1, 2] The thermoelectric performance of TE materials is generally determined by the figure of merit  $ZT=S^2\sigma T/\kappa$ , where parameters in numerator *S*,  $\sigma$  and *T* are the Seebeck coefficient, electrical conductivity, and absolute temperature, respectively, and  $\kappa$  in the denominator is the thermal conductivity.[3-5] Maximizing power factor ( $S^2\sigma$ ) and minimizing  $\kappa$  are two basic approaches to obtain high *ZT* values. Various strategies such as increasing carrier effective mass,[6] modulation doping,[7] synergistic alloying,[8] and constructing all-scale hierarchical architectures,[9] have been performed and made progress in improving the TE performance of materials.

Additionally, low-dimensional structured, containing nanostructured thin films can significantly enhance *ZT* of TE materials due to the reduction of the phonon thermal conductivity while improving or even maintaining the electronic transport by interface energy filtering or quantum confinement.[10-14] Recently, due to the rapid rise in the demand for wearable and portable electronics, nanostructured TE thin films have attracted more and more attention with the potential in fabricating various miniaturized and flexible TE devices. From now, low-cost and non-toxic TE thin films with high TE performance are highly desired in practical applications.

Skutterudite bulk CoSb<sub>3</sub> TE material is considered as one of the most promising candidates for TE power generations which has been widely investigated due to their excellent TE properties, relatively low-cost, and abundant constituent elements.[15-19] In the lattice of Skutterudite CoSb<sub>3</sub>, there exist two interstitial sites naturally and extraneous atoms can fill those. The filled atoms act as "rattling" centers and scatter the phonons, resulting in a dramatic decline in  $\kappa$ . For instance, Zhao et al.[19] reported Yb-filled CoSb<sub>3</sub> composite with significant enhanced *ZT* of 1.3 due to considerable scattering of phonons with very slightly disturbing electron transport, caused by a combined effect from dispersed Yb<sub>2</sub>O<sub>3</sub> nanoparticles at/within grain boundaries with a slight impact on electron transport. Based on a similar idea, a (GaSb)<sub>0.2</sub>/Yb<sub>0.26</sub>Co<sub>4</sub>Sb<sub>12</sub> nanocomposite further improved the peak *ZT* up to 1.45 at 850 K.[18] Analogously,

various processing techniques, such as molecular beam deposition,[20] magnetron sputtering deposition,[21-23] electrochemical synthesis,[24] and pulsed laser deposition,[25] have been performed to fabricate CoSb<sub>3</sub> thin films. Particularly, magnetron sputtering at radio frequency (RF) is a facile method to deposit thin films of high quality for the industrial community. In our previous work, Ag-doped CoSb<sub>3</sub> films with good crystallinity have been successfully prepared by employing magnetron sputtering method, where the Ag atoms effectively fill in the interstitial sites, causing the enhanced electrical transport properties of CoSb<sub>3</sub> films.[21, 22] The maximum  $S^2\sigma$  of 0.27 mW m<sup>-1</sup> K<sup>-2</sup> at 600 K was achieved, which is twice than that of the un-doped.[21] However, only a few thin-film studies with enhanced *ZT* values have been reported, and the TE performance of thin film is still far behind those of filled CoSb<sub>3</sub> bulks.[18-20]

In this work, we employ a simple and robust *in-situ* growth method to fabricate CoSb<sub>3</sub> thin films. (Ag, Sn) co-doped CoSb<sub>3</sub> thin films are *in-situ* grown by using co-sputtering of Ag and CoSb<sub>3</sub> on the Sn metallic precursor layer.(Fig. S1) Both Ag and Sn are considered to be commendable n-type dopants for optimizing TE properties of the as-prepared CoSb<sub>3</sub> thin films.[26-28] To precisely control the composition and microstructures of co-doped CoSb<sub>3</sub> films, the Ag and Sn are introduced by subsequent using of co-sputtering process and layer diffusion process, respectively. As a result, all the as-prepared films consist of single-phase CoSb<sub>3</sub> with nano-size grains. Such (Ag, Sn) co-doped CoSb<sub>3</sub> thin films process a reduced  $\kappa$  of 0.28 W m<sup>-1</sup> K<sup>-1</sup> and an increased *ZT* of ~0.52 at 623 K. This work indicates that our in-situ method can be used for high-performance TE thin films, which shows great potential to apply for the miniature thermoelectric devices.

#### 2. Experimental

The (Ag, Sn) co-doped CoSb<sub>3</sub> thin films are deposited by using the magnetron sputtering which had been performed in our previous works.[21, 22] High purity Ag (99.99 %), Sn (99.99 %), and CoSb<sub>3</sub> (99.95 %) alloy targets were fixed in a deposition chamber with a three-targets system. The BK7 glass substrates with a dimension of 2 mm  $\times$  2 mm  $\times$  1.5 mm were sequentially cleaned in the ultrasonic bath with acetone,

deionized water, and ethanol. The chamber background pressure was maintained at  $8.0 \times 10^{-4}$  Pa while the working pressure was maintained at 0.4 Pa with the Ar flow rate of 40 Sccm. A schematic view of the preparation details is shown in Supplementary Information (Fig. S1). At first, the Sn precursor layer was deposited by the RF magnetron sputtering on the glass substrate with ~ 50 nm/min deposition rate. Adjustment of the deposition time (10s, 15s and 20s) was done to control the rate of Sn deposition for this precursor layer. Then, the Ag-doped CoSb<sub>3</sub> layer was deposited onto this precursor layers under 250 °C in a co-sputtering process with 50 W sputtering power for 30 min. The power and the duration of sputtering for the Ag target were selected to be 1 W and 10 s, respectively.

X-ray diffraction (XRD) (D/max 2500 Rigaku Corporation, CuK<sub>α</sub> radiation from  $10^{\circ}$  -  $80^{\circ}$  angle under  $0.02^{\circ}$  per step) was applied to analyze the crystal orientation of the CoSb<sub>3</sub> films. The full-profile Rietveld refinement method was utilized to analyze the lattice parameters. The surface morphology and element distribution were characterized by a scanning electron microscope (SEM, Zeiss supra55) with an energy dispersive spectrometer (EDS). The Raman scattering measurements were performed using a spectra system Lab Xplora (Horiba Jobin Yvon). The S and  $\sigma$  were measured at the temperature range from 300 K to 623 K using an electrical conductivity and Seebeck coefficient apparatus (SBA458, Nezsch). By the laser flash method (TF-LFA, Germany), the thermal diffusivity D was measured. Prior to the measurements, the thin films were deposited with a Ti layer of ~10 nm and an Au layer of ~200 nm. The  $\kappa$  were calculated by using the equation  $\kappa =$  $D\rho C_p$ ,[29] where  $\rho$  is the density and  $C_p$  is the specific heat capacity obtained from bulk CoSb<sub>3</sub>. Van der Pauw Hall measuring instrument (HL5500 PC, Nanometrics) was applied to investigate the carrier concentration and the mobility evolution. The band gaps of the films were measured by a LAMBDA 950 UV/VIS/NIR spectrophotometer. Carrier concentration n was obtained from Hall effect measurements (HL5500PC, Nanometrics), the mobility ( $\mu$ ) was calculated by  $\mu = \sigma R_{\rm H}$ . Nanoindentation experiments[30, 31] were performed on the sample by using Nanoindenter XP (MTS). We used an array of  $10 \times 10$  indents, each 1 mm in depth, using the continuous

stiffness measurement (CSM) method. In this work, the uncertainty of carrier concentration and carrier mobility is about 10%. While the combined uncertainty for the experimental determination of ZT is about 15% and is caused by the measurements including electrical conductivity, Seebeck coefficient, thermal diffusion coefficient, thermal capacity, and density. The uncertainty of elastic modulus and hardness is about 10%.

The electron interaction, a plane-wave expansion, atomic structure were analyzed by using a first-principle density-functional theory (DFT) as implemented in the code Vienna Ab-initio Simulation Package (VASP).[32] To simplify the calculation, the defect-controlled electronic structure was neglected. The electron interaction between the valence electron and ionic cores were described by the pseudopotentials. Perdew Burke Ernzerhof (PBE) parameters were applied to represent the electron exchange and correlation potential.[33] Energy calculations were performed on a  $4 \times 4 \times 3$  high-symmetry *k*-point grid in the Brillouin zone. The convergence threshold conditions are a maximum energy evolution of  $2.0 \times 10^{-5}$  eV and a maximum force below 0.02 eV/Å.<sup>[34]</sup>

#### 3. Results and Discussion

Figure 1 (a) is the XRD patterns of Ag and Sn co-doped CoSb<sub>3</sub> thin films in a  $2\theta$  range from 20° to 80°. As can be seen, the diffraction peaks are well indexed to the standard skutterudite CoSb<sub>3</sub> structure with a *Im3* space group (PDF#78-0976) [35], and the absence of any impurity phase obvious for all XRD patterns, indicating all the films possess a CoSb<sub>3</sub> phase with high-purity. Debye-Sheerer equation was used to estimate the grain size of the films with and without doping.[36] The un-doped film has an average grain size of ~230 nm, and it further increases to ~260 nm, 280 nm, and 290 nm with the increase of Sn content of 1.7 %, 2.3 %, and 3.2 %, respectively. Here, the chemical compositions are analyzed by SEM-EDS and results are summarized in Table S1. On the other hand, from the magnified XRD patterns and Fig. 1(b), it can be observed that peak (013) gradually shifts toward to the smaller angle with increasing Sn content, which corresponds to the enhancement of lattice parameters. Besides, the lattice parameters display a non-linear expansion, suggesting

that the extraneous Ag and Sn atoms tend to fill into the interstitial sites.[34, 37] These results are in good agreement with the non-linear expansion phenomenon of the lattices reported for  $Yb_yCo_4Sn_xSb_{12-x}$  and  $Br_xCo_4Sb_{12}$  samples,[14, 34] in which both Yb and Br are preferred to fill the interstitial sites. Takizawa et al.[38] also reported that the Sn atoms enter into the interstitial sites of the CoSb<sub>3</sub> rather than frame sites for Sn<sub>x</sub>Co<sub>4</sub>Sb<sub>12</sub>.

To confirm the doping states of the Ag and Sn, we performed DFT calculations for the confirmation of Ag and Sn doping states in the films. Fig. 1 (c) shows the calculated formation energies in different doping states of Ag and Ag/Sn, including occupying Sb sites, occupying Co sites, and interstitial sites. The corresponding crystal structures are shown in the inset figures, which display the occupied states. It can be observed that among the different situations of Ag, Sn, and Ag/Sn co-doping the lowest formation energy is possessed by the interstitial state. This corresponds well with the XRD results that Ag, Sn atoms prefer to form interstitial states inside the CoSb<sub>3</sub> structure. We also investigated the structural variations of co-doped films by Raman spectrometry. For as-prepared (co-doped) thin films, Fig. 1 (d) shows Raman scattering spectra from 100 cm<sup>-1</sup> to 200 cm<sup>-1</sup> range. There are four sharp peaks of Raman sensitive phonon vibration modes observed in the Raman scattering spectra, which can be identified as  $F_{g2}$ ,  $E_{g1}$ ,  $E_{g3}$ , and  $E_{g2}$ , in which  $E_g$  ( $E_{g1}$  and  $E_{g2}$ ) mode is Raman active with polarizability tensor component while the  $F_g \ (F_{g1} \ and \ F_{g2})$  is "orthogonal" to Eg as predicted with the theoretical simulation.[39] The absence of any extra peaks confirms the single cubic structure of the films. Moreover, the full width at half maximum and the relative intensity are almost the same before and after doping, suggesting that CoSb<sub>3</sub> possesses a stable bonding state. A slight shift in F<sub>g2</sub> and  $E_{g3}$  vibration modes is observed which can be attributed to the dynamic disorder aroused by Ag and Sn atoms insertion in the lattice.



**Fig. 1** (a) XRD patterns of CoSb<sub>3</sub> thin films. The right side is showing the patterns of (013) peaks with magnified XRD. (b) Influence of Sn doping content on the Lattice parameters. (c) Calculated formation energies of Ag, Sn, and Sn/Ag co-doping in different states of doping. The corresponding doping states are illustrated in Figure S2. (d) Raman spectra of un-doped and Ag/Sn co-doped CoSb<sub>3</sub> based thin films.

Fig. 2(a-d) show the surface morphology of the thin films. The flat and smooth surface as well as some crystals are also observed in the un-doped sample (Fig. 2a), suggesting that the undoped sample consists of crystalline grains. As Sn content (for instance, Sn content 1.7 %) doped in thin films, it is observed that some small grains are located around many large grains (with an average size of 240 nm). The grains size increase with the increase of Sn doping content as shown in Fig. 2(b-d). For the sample with a Sn content of 2.3 %, the tiny grains and the larger CoSb<sub>3</sub> grains (the size less than 300 nm) are uniformly distributed on the film surface, and the element mapping results as shown in Fig. S3 indicates that all the elements are homogeneously distributed. The good quality of crystallization after doping of Ag and Sn is conducive

to the transfer of carriers and leading to the enhancement of carrier mobility. With the increase of Sn content up to 3.2 %, the size of larger grains increases over 400 nm. The mechanism of coexisting two different sizes of grains during the growth of the thin film is illustrated in Fig. 2(e). At first, the Sn layer is formed in Volmer-Weber growth mode, then two-dimensional growth of Sn layer was performed with island-like structure (Fig. 2(e) - (1)). This island-like structure will lead to the different growth rates during the co-sputtering of Ag and CoSb<sub>3</sub> under the high substrate temperature of 250 °C. Thus, by controlling the thickness of the Sn precursor layer, the grain size of CoSb<sub>3</sub> films can be optimized.



**Fig. 2** SEM images of (a) un-doped, (b) 0.2 % Ag + 1.7 % Sn co-doped, (c) 0.2 % Ag + 2.3 % Sn co-doped, and (d) 0.2 % Ag + 3.2 % Sn co-doped CoSb thin films. (e) Schematic illustration of CoSb} growth (1) Sn layer deposited on the substrate; (2) Formation of (Ag, Sn) co-doping CoSb} films ;(3) Distribution of grains in CoSb} films.

Fig. 3(a) presents the HADDF-STEM image for 0.2 % Ag with 2.3 % Sn co-doped CoSb<sub>3</sub> based thin film, no element segregation is detected in as-prepared CoSb<sub>3</sub> based thin film. The lattice spacing measurement in Fig. 3(a) corresponds with CoSb<sub>3</sub> crystal showing a well-crystallized and homogeneous CoSb<sub>3</sub> base film frame structure where frame atoms (Co, Sb) and atomic columns of the filler (Ag/Sn) are

clearly distinguishable (as shown in Fig.3(c) & 3(d)). However, one can obviously notice some secondary phases as marked by red dashed circles in Fig. 3(a) and 3(b). In addition, TEM-EDS confirms that these secondary phases are Ag-rich co-doped CoSb<sub>3</sub> phase, as given Fig. S4. The observed nano-sized Ag-rich secondary phases exhibit a circular shape with a diameter of ~10 nm embedded in the Ag/Sn doped CoSb<sub>3</sub> matrix. These nano-sized areas are clearly distinguishable separating the Ag-rich nanophase and the doped matrix. Therefore, it can be seen that micrographs of the matrix (Fig. S2 & Fig. 3d (an IFFT image of white dashed square area of inset b1 in Fig. 3(b))) and of the nano-sized phase (Fig. S3 & Fig. 3d (an IFFT image of yellow dashed-square b2 in Fig. 3(b))) indicate that nano-phase being a Ag-rich phase possesses CoSb<sub>3</sub> frame structure filled with more Ag atoms as filler atoms in the interstitial sites of CoSb<sub>3</sub> frame while the CoSb<sub>3</sub> matrix being low in Ag phase retains CoSb<sub>3</sub> frame structure filled with (Ag/Sn) filler atoms in the interstitial sites of the frame structure. Moreover, Ag is likely more favorable to form in-situ Ag-rich nanophase to achieve charge compensation in the vicinity of dispersed filler atoms and cause the lattice distortions which can be frequently observed in Fig. 3(f). Fig. 3(g) is showing the evidence with inset presenting the Inverse Fast Fourier transformation (IFFT) pattern. Notably, the high density of lattice distortions easily forms in co-doped CoSb<sub>3</sub> thin film, especially co-doping leads to the formation of the Ag-rich nano-phases. Fig. 3(f) & 3(g) clearly show the sizes of these lattice distortions, which indicate the interstitial doping of Ag and Sn have induced the significant lattice strain which causes to enhance the phonon blocking, as shown in Fig 3(f)-(k). Since, as described earlier, a high density of lattice distortions coupled with nano-sized Ag-rich grains can greatly enhance phonon scattering so as to effectively reduce thermal transportation.



**Fig. 3** STEM-HAADF image of the thin film with 0.2 % Ag + 3.2 % Sn; (a)-(b) images indicate the distribution of grain boundaries and nano-sized Ag-rich precipitates, c) schematic view of co-doped CoSb<sub>3</sub> frame structure, (d)-(e) corresponding IFFT images of the area spotted in rectangle b1 & b2 in (b), (f) lattice distortion cores embedded in HRTEM image acquired from co-doped CoSb<sub>3</sub> thin film,(g) Inverse FFT (IFFT) image of the area spotted in solid rectangle 1 in (f) and inset are the enlarged view of solid rectangle regions (b1) & (b2) in (g), (h) IFFT image of the area spotted in solid rectangle 2 in (f), (i)-(k) strain mapping of areas spotted in dashed rectangles b1, b2 & c1 in (g) and (h) showing the embedded lattice distortions, respectively.

Fig. 4 shows the temperature-dependent TE properties of the (Ag, Sn) co-doped CoSb<sub>3</sub> thin films. As shown in Fig. 4(a),  $\sigma$  of the un-doped CoSb<sub>3</sub> film is ~ 1600 S m<sup>-1</sup> at 298 K, while  $\sigma$  increases up to ~2000 S m<sup>-1</sup> with the doping of Ag and Sn. During the measured entire temperature range, all the  $\sigma$  values present an increasing trend with increasing temperature, indicating a semiconductor behavior. The film with 0.2 % Ag + 1.7 % Sn shows the highest  $\sigma$  value of 6400 S m<sup>-1</sup> at 623 K, which is

36.2 % higher than that of the un-doped film at the same temperature. The optimization of  $\sigma$  after Ag doping in CoSb<sub>3</sub> is mainly due to the improvement of *n*.[21, 22] Therefore, to further investigate the effect of Sn doping on electrical transport properties, we further performed the Hall measurement on un-doped and (Ag, Sn) co-doped CoSb<sub>3</sub> thin films.  $\sigma$  was analyzed by the formula  $\sigma = n\mu e$ , where e is the electron charge. Fig. 4(b) presents that the variation of n and  $\mu$  with different Sn contents. With the increase of Sn doping content, n gradually decreases from ~24  $\times$  $10^{20}$  cm<sup>-3</sup> for the un-doped sample to  $4.0 \times 10^{20}$  cm<sup>-3</sup> for the sample with 0.2 % Ag + 3.2 % Sn film. The decrease of n is related with the lattice distortions formed in co-doped  $CoSb_3$  thin film which originates from the occupation of Ag and Sn in interstitial sites of CoSb<sub>3</sub> lattice. Therefore, with further increasing the Sn-doping content, the rise in  $\mu$  is possible on the cost of n, as the scatterings between carriers become weaken. Thus, the boost in  $\sigma$  majorly attributed to the raise of  $\mu$ . Fig. 3(c) shows the temperature-dependent S for un-doped and co-doped CoSb<sub>3</sub> based thin films. A typical *n*-type behavior is obvious from the negative values of S. S of all the samples presents the increasing trend with increasing the temperature. For 0.2 % Ag doped CoSb<sub>3</sub> film, the absolute S is enhanced to ~40  $\mu$ V K<sup>-1</sup> at 298 K,[22] the absolute S is further improved to ~ 50  $\mu$ V K<sup>-1</sup> for the Ag and Sn co-doped films, which is over twice of un-doped CoSb<sub>3</sub> based film. The variation observed in S agrees with the decline in *n* (Fig. 4(b)). The maximum absolute S of ~ 220  $\mu$  K<sup>-1</sup> for 0.2 % Ag + 1.7 % Sn film is obtained at 623 K, which is 21.8 % higher than the un-doped film. Combining the results of  $\sigma$  and S, the estimated  $S^2\sigma$  for un-doped and co-doped films are shown in Fig. 4 (d). Due to S and  $\sigma$  coupling optimization, the S<sup>2</sup> $\sigma$  values of all Ag and Sn co-doped CoSb<sub>3</sub> based thin films exhibit higher values than the un-doped CoSb<sub>3</sub> thin film over the whole measurement temperature range. At 623 K, the maximum  $S^2\sigma$  of 0.31 mW m<sup>-1</sup> K<sup>-2</sup> is achieved for 0.2 % Ag + 1.7 % Sn film, which is over two times than that of pristine CoSb<sub>3</sub> thin film.



Fig. 4 (a) Temperature dependence of  $\sigma$  of the CoSb<sub>3</sub> thin films. (b) Measured *n* and  $\mu$  of the thin films as a function of Sn doping content. (c) Temperature dependence of *S* and (d)  $S^2\sigma$  of the CoSb<sub>3</sub> thin films.

To further explain the unique electrical transport performance of (Ag, Sn) co-doped CoSb<sub>3</sub> thin films, first-principles DFT calculations were performed. Fig. 5(a-b) show the calculated band structures of un-doped, and interstitially Ag/Sn co-doped CoSb<sub>3</sub>, respectively. It can be seen that the Fermi level is located at the center of the bandgap of the un-doped films. While the Fermi level position moves into the conduction band after interstitially Ag/Sn co-doped CoSb<sub>3</sub>, which is beneficial to the transport of electrons and enhancement of  $\sigma$  value. In addition, the conduction band minimum and valence band maximum are in the same  $\tau$  - point, indicating the direct band gaps for un-doped and co-doped films.[40, 41] As shown from the Fig. 5(a-b), the direct band gaps of the un-doped and co-doped films are 0.17

eV and 0.22 eV, respectively, suggesting the increase of bandgap after co-doping of Ag and Sn. Fig. 5(c-d) present the DOS of un-doped and Ag/Sn co-doped CoSb<sub>3</sub>, respectively. The *TE* performances of CoSb<sub>3</sub> based thin film are mainly affected by the total and partial density of states (DOS) near the Fermi level.[41] After co-doped of Ag and Sn, an impurity band was induced (Fig. 5(b)), which indicates that the highly dispersive bands at  $\Gamma$  are much more spatially delocalized (Fig. 5(a). The total DOS and partial DOS (PDOS) for interstitially Ag/Sn co-doped CoSb<sub>3</sub> as shown in Fig. S6 further confirmed the increased DOS intensity near Fermi level majorly comes from Sb partial DOS. The relationship of DOS and *TE* properties of Cosb<sub>3</sub> based thin films can be investigated by the Mott formula as introduced in equation (1),[41] in which the *S* is proportional to the derivative of the log DOS at Fermi energy.

$$S = \frac{\pi^2 k_B^2 T}{3q} \left\{ \frac{dg(e)f(e)}{ndE} + \frac{d\mu(e)}{\mu dE} \right\}_{E=E_F}$$
(1) (1)

where  $k_B$ , *T*, g(e), f(e),  $\mu(e)$ , *n*,  $E_F$  is Boltzmann constant, temperature, the density of state, Fermi function, mobility, electron charge, Planck constant, carrier concentration, and Fermi level, respectively. After the Ag and Sn co-doping, the enhancement in the DOS near to the Fermi energy is beneficial to the improvement of *S*, the calculated results are in good agreement with that of the experimental results.



**Fig. 5** Calculated band structures of (a) pristine and (b) Ag/Sn co-doped CoSb<sub>3</sub> and corresponding DOS & PDOS of (c) pristine and (d) Ag/Sn co-doped CoSb<sub>3</sub>, respectively.

In this work, the CoSb<sub>3</sub> based thin films are considered as isotropous materials as CoSb<sub>3</sub> possesses a cubic structure.[42] Fig. 6 (a) shows the temperature-dependent  $\kappa$  of (Ag, Sn) co-doped CoSb<sub>3</sub> thin films. The  $\kappa$  values greatly decrease from ~2.20 W m<sup>-1</sup> K<sup>-1</sup> for un-doped CoSb<sub>3</sub> to ~0.55 W m<sup>-1</sup> K<sup>-1</sup> for co-doped samples with 0.2 % Ag and 3.2 % Sn at 375 K (Fig. 6(a)). Furthermore, the minimum  $\kappa$  reaches ~0.28 W m<sup>-1</sup> K<sup>-1</sup> at 623 K for 0.2 % Ag + 1.7 % Sn film. The  $\kappa_l$  was obtained from the difference between the  $\kappa$  and  $\kappa_e$  (where  $\kappa_e$  is calculated by Wiedemann–Franz law  $\kappa_e = L\sigma T$ ,[43] *L* is the Lorenz number), and plotted in Fig. 5(b) for exploring the fundamental reason behind the reduction in  $\kappa$ . The calculated *L* values and  $\kappa_e$  were plotted in Supporting Information (Fig. S5). It can be seen that  $\kappa_e$  (Fig. S5(b)) is much smaller that of  $\kappa_l$  (Fig. 6(a)), indicating that  $\kappa$  is mainly determined by  $\kappa_l$ . As it can be seen in Fig. 6(b),  $\kappa_l$ almost shares the same value with  $\kappa$ , confirms that it is playing the main role behind the low  $\kappa$  in both the un-doped and the co-doped films. In the co-doped films, the observed phonon scattering sources are illustrated in the insets. The significant reduction in  $\kappa_l$  for the co-doped film can attribute to the point defects due to interstitial atoms of Ag/Sn and Sb vacancies that are the cause of short-wavelength phonons scattering, and a high density of lattice distortions coupled with nano-sized Ag-rich grains can greatly enhance scattering of medium and long-wavelength phonons.



**Fig. 6** Temperature dependence of (a)  $\kappa$ , (b)  $\kappa_l$ , (c) *ZT* of the thin films. (d) Comparison of *ZT* values among Yb-filled CoSb<sub>3</sub>,[44] pristine CoSb<sub>3</sub>,[45] and CoSb<sub>3</sub> based thin films in this work. (e) Displacement as a function of loading force during a cyclic test of un-doped and co-doped CoSb<sub>3</sub> thin films, with 0.2 % Ag and 2.3 % Sn. (f) Elastic modulus and hardness of un-doped and co-doped CoSb<sub>3</sub> thin films, with 0.2 % Ag and 2.3 % Sn.

The calculated ZT values of (Ag, Sn) co-doped CoSb<sub>3</sub> thin films are shown in Fig. 6 (c). The ZT values are significantly enhanced after co-doping of Ag and Sn due to the optimizing electrical and thermal transports, synergistically. As a result, a high ZT value of ~0.52 is obtained for the CoSb<sub>3</sub> films with 0.2 % Ag + 2.3 % Sn and 0.2 % Ag + 3.2 % Sn co-doping at 623 K, which is clearly higher than that of other previously reported CoSb<sub>3</sub> films, such as the Yb-filled CoSb<sub>3</sub> fabricated by DC-sputtering method including Yb-filled CoSb<sub>3</sub>[44], pristine CoSb<sub>3</sub>[45] prepared by chemical vapor deposition as shown in Fig. 6(d). Apart from the achieved high TE performance in the present system, the mechanical properties also play an important role for TE applications due to the requirement of the manufacturing process and operational durability. Therefore, we further explored the mechanical performance test by a nanoindentation measurement on un-doped and co-doped thin films, with 0.2 % Ag and 2.3 % Sn. Fig. 6 (e) shows the displacement as a function of loading force for two samples during a cyclic test. As it can be seen that the films with 0.2 % Ag and 2.3 % Sn can bear more stress than that of un-doped film, indicating better mechanical properties of co-doped samples. Actually, both Young modulus and hardness of co-doped sample enhanced after Ag and Sn doping as shown in Fig. 6(d), which increased from ~92 GPa and 7.3 GPa for un-doped CoSb<sub>3</sub> film to ~102 GPa and 9.2 GPa for the sample with 0.2 % Ag and 2.3 % Sn, respectively. Thus, the good mechanical properties of co-doped CoSb<sub>3</sub> film are beneficial for fabricating high TE performance with high thermoelectric modules.

## 4. Conclusions

(Ag, Sn) co-doped CoSb<sub>3</sub> thin films are fabricated via a facile *in-situ* growth process, in which Ag and CoSb<sub>3</sub> are co-sputtered on the Sn metallic precursor layer. The as-prepared thin films consist of single-phase CoSb<sub>3</sub> with nano-sized grains. The theoretical calculations and experimental results indicate that Ag, Sn atoms trend to enter the lattice and preferentially filled interstitial sites. The increase in  $\sigma$  and *S* are observed after co-doping of Ag, Sn, which can be well explained by the band structure calculations that the Fermi level moves into the conduction bands and increases the density of state. An extremely low  $\kappa$  of ~0.28 W m<sup>-1</sup> K<sup>-1</sup> is achieved due to the all-scale phonons scattering by multiple microstructures including point defects from interstitial atoms of Ag/Sn and Sb vacancies, lattice distortions, and nano-sized Ag-rich grains. As a result, a maximum *ZT* value ~0.52 at 623 K for co-doped CoSb<sub>3</sub> film with 0.2 % Ag and 2.3 % Sn. Young modulus and hardness of co-doped sample greatly enhanced after Ag and Sn doping, indicating its potential to apply for miniature thermoelectric devices.

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