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Citation: [Journal of Applied Physics](#) **110**, 083710 (2011); doi: 10.1063/1.3651382

View online: <http://dx.doi.org/10.1063/1.3651382>

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Lattice dynamics and substrate-dependent transport properties of (In, Yb)-doped CoSb₃ skutterudite thin films

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(Received 18 July 2011; accepted 5 September 2011; published online 24 October 2011)

Lattice dynamics, low-temperature electrical transport, and high-temperature thermoelectric properties of (In, Yb)-doped CoSb₃ thin films on different substrates are reported. Pulsed laser deposition under optimized conditions yielded single-phase polycrystalline skutterudite films. Raman spectroscopy studies suggested that In and Yb dopants occupy the cage sites in the skutterudite lattice. Low-temperature electrical transport studies revealed the *n*-type semiconducting nature of the films with extrinsic and intrinsic conduction mechanisms, in sharp contrast to the degenerate nature reported for identical bulk samples. Calculations yielded a direct bandgap close to 50 meV with no evidence of an indirect gap. The carrier concentration of the films was identical to that reported for the bulk and increased with temperature beyond 250 K. The higher resistivity exhibited is attributed to the enhanced grain boundary scattering in films with a high concentration of grains. The maximum power factor of $\sim 0.68 \text{ W m}^{-1} \text{ K}^{-1}$ obtained at 660 K for the film on glass is found to be nearly four times smaller compared to that reported for the bulk. The observed difference in the power factors of the films on different substrates is explained on the basis of the diffusion of oxygen from the substrates and the formation of highly conducting CoSb₂ phase upon the oxidation of CoSb₃. © 2011 American Institute of Physics. [doi:10.1063/1.3651382]

I. INTRODUCTION

CoSb₃-based skutterudites have been attracting considerable research interest owing to their high Seebeck coefficient (α) and high electrical conductivity (σ).^{1–4} The complex crystal structure of CoSb₃ provides a favorable framework to reduce the otherwise larger thermal conductivity (κ) of CoSb₃ and enhance the dimensionless thermoelectric figure of merit, $ZT = \alpha^2 \sigma T / \kappa$. The desirable reduction in thermal conductivity can be achieved by filling the two naturally formed voids in CoSb₃ with guest atoms that can substantially impede the lattice phonon propagation.^{5–10} The weak interaction between the guest atom and the host lattice enables incoherent rattling motion of the guest species. Generally, the rattling frequency is not unique and, hence, the guest atoms are treated as classical Einstein oscillators.¹¹ The low-frequency rattling of the guest atom effectively scatters the acoustic phonons without significantly altering the electrical properties and, hence, enhances the ZT . Hence, filled skutterudites form a class of phonon-glass electron-crystals (PGEC),^{12,13} which are promising candidates for efficient thermoelectric energy conversion. The scattering of phonons is found to be more pronounced in double-filled skutterudites, wherein the filler atoms are distinct in size and atomic weight, so as to facilitate dual-frequency resonant scattering.^{14–16} Recently, high ZT has been demonstrated in bulk (In, Yb)-doped CoSb₃ grown by spark-plasma sintering.^{14,17,18} The incorporation of In and Yb is reported to help reduce the lattice thermal conductivity without significantly

altering the power factor ($\alpha^2 \sigma T$), thereby resulting in an enhanced ZT as compared to undoped CoSb₃.¹⁷

Further reduction in lattice thermal conductivity is possible in thin films because interfaces and grain boundaries in low-dimensional systems effectively scatter phonons.^{19,20} It will be of both fundamental and practical significance to examine the thermoelectric properties of thin films of (In, Yb)-doped CoSb₃ on different substrates of practical significance. Moreover, the available reports on the growth,^{21–23} transport, and structural properties^{24–27} are either limited to CoSb₃ films or on thermoelectric properties of filled CoSb₃ films.²⁷ For instance, Caylor *et al.*²² and Colceag *et al.*²⁸ have studied the influence of growth conditions on the phase purity, crystallinity, and morphology of CoSb₃ thin films grown by pulsed laser deposition (PLD). Savchuk *et al.*²⁴ have studied the carrier transport mechanisms in CoSb₃ thin films grown by dc magnetron sputtering. Song *et al.*¹⁹ have analyzed the influence of different scattering mechanisms on the significant reduction in thermal conductivity of PLD grown CoSb₃ thin films and superlattices as compared to the bulk. Ziepl *et al.*²⁷ have reported high electrical resistivity in Yb-doped CoSb₃ films grown by PLD, but no physical explanation was provided. Similarly, lattice dynamics of skutterudites have been studied by *ab initio* methods, inelastic x-ray scattering,¹¹ and Raman spectroscopy.^{29–31} Raman spectroscopy studies on skutterudites however are limited to undoped and filled CoSb₃ bulk materials, and hardly any reports are available on Raman scattering studies of filled or unfilled CoSb₃ thin films. It is important to identify whether the dopant atoms enter the void structure of CoSb₃ or substitute the lattice points. Presence of InSb and Yb₂O₃ secondary phases have been recently reported in CoSb₃ bulk materials filled

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with (In, Yb) casting doubt on whether all the dopants indeed occupy the cage positions. Raman spectroscopy studies of (In, Yb)-doped CoSb₃ films may help resolve this to a larger extent.

Recently, we have reported the high-temperature thermoelectric properties of (In, Yb)-doped CoSb₃ films grown by PLD.³² Detailed studies on the conduction mechanisms of (In, Yb)-doped CoSb₃ are important from both a fundamental and applications point of view of this important class of thermoelectric materials. In this work, we report the lattice dynamics and transport properties of (In, Yb)-doped CoSb₃ thin films grown under optimized conditions on four different substrates and analyze the high-temperature thermoelectric properties of the films on the basis of diffusion of oxygen across the film-substrate interface.

II. METHODS

A. Growth of films

The films were deposited using PLD of spark plasma sintered (In, Yb)-doped CoSb₃ target (In_{0.1}Yb_{0.1}Co₄Sb₁₂). The details of the synthesis of the target can be found elsewhere.¹⁴ The PLD growth chamber was evacuated to $<10^{-7}$ Torr, and 10 mTorr of argon gas was allowed into the chamber prior to deposition. The introduction of argon is expected to result in a better thermalization of the species in the ablation plume. The target-substrate distance was held fixed at 9 cm. All the different substrates were held using silver paste to a rotating substrate holder having a radiant heater arrangement. The use of silver paste is reported to reduce isotropic compressive stresses that cause blistering of the surface of CoSb₃ films.²⁸ The large target-substrate distance, the presence of argon gas, and the use of silver paint ensured that all the grown films were free of blistering.

A KrF excimer laser (248 nm) with pulse duration of 20 ns and repetition rate of 10 Hz was used for ablation. An optimized laser fluence of 260 mJ/pulse (corresponding to an energy density of 4.6 J/cm²) was found to be above the ablation threshold. Films were deposited on glass (Fisher Scientific, USA), single-crystal quartz (X-cut, MTI Corporation, USA), $\langle 100 \rangle$ oriented MgO (MTI Corporation, USA), and thermally grown amorphous SiO₂ covered Si (Si/SiO₂) substrates maintained at a temperature of 533 K. The number of shots was limited to 20,000 for all the films and, hence, the thickness of the films was fixed (~ 200 nm). The films grown under the optimized conditions were subjected to a heat treatment in argon ambient for 14 h, wherein the temperature of the furnace was slowly ramped to 700 K and cooled to room temperature. The surface roughness of the as-deposited films was ~ 3 nm and increased to ~ 14 nm upon heat treatment.³² All the studies reported in this work were performed on the heat-treated films.

B. Characterization, electrical transport, and thermoelectric measurements

Grazing incidence x-ray diffraction (GIXRD) measurements were carried out using D8 Discover, Bruker AXS (Germany) on the films at a grazing angle of 0.5° to analyze

the phase purity of the films. Raman Spectroscopy was used to verify the phonon frequencies of the films. Raman spectra were acquired using a confocal Raman spectroscope (Lab-RAM ARAMIS, Horiba-Jobin Yvon, USA) equipped with holographic gratings of 1800 grooves/mm. The 488-nm line of an Ar⁺-ion laser was used for excitation. The spectral resolution used was ~ 1 cm⁻¹. Scanning electron microscopy (SEM) equipped with energy dispersive analysis by x rays (EDAX) and electron energy-loss spectroscopy (EELS) was used to identify the chemical composition of the films as well as to probe the interface of the films with the substrates. EDAX spectra were obtained from different areas of the films and the composition of the films was determined after applying suitable ZAF corrections to the data (Z is the atomic number of the material, A is absorption, and F is fluorescence). Co and O core-loss signal intensity is measured along an EELS line scan perpendicular to the interface to gather information pertaining to the interface. The length of the scan lines is varied until stable signals of Co and O are obtained on either side of the physical interface.

Low-temperature electrical conductivity and Hall Effect were measured in the temperature range from 5 to 350 K on a Physical Property Measurement System (PPMS, Quantum Design) using a four-probe configuration. The magnetic field was swept between ± 5.0 T at each temperature to obtain a slope leading to the Hall coefficient, R_H . By assuming a simple band model, the carrier concentration was estimated using the relation $n = -1/(eR_H)$. Employing the linear four-probe and differential methods, respectively, high-temperature electrical conductivity and Seebeck coefficient of the films were measured in the temperature range from 300 to 660 K using a Seebeck tester (Ozawa RZ2001i). For the Seebeck coefficient measurement, the typical temperature difference was limited to the range 2–6 K.

III. RESULTS AND DISCUSSION

A. Characterization: GIXRD and EDAX

The phase purity of the films was verified by GIXRD. Figure 1 shows the GIXRD pattern, together with the θ - 2θ pattern for the target. Films on the different substrates show identical GIXRD patterns. Similar to the target, the films are polycrystalline and single-phase in nature and the peaks could be indexed based on the cubic structure of CoSb₃ (space group: Im-3, number 204). Any trace secondary phases that may be present in the film are beyond the detection limit of GIXRD. The lattice constant of the films and the target is 9.131 Å, and lies between the reported values for bulk cubic CoSb₃ (9.12 Å) and In_{0.25}Yb_{0.25}Co₄Sb₁₂ (9.158 Å).³³ The mean crystallite size of the films calculated using Scherrer formula is ~ 40 nm. EDAX was performed on different regions of the films, and the results showed that the nominal composition of the films was roughly 2.4 at. % In, 2.7 at. % Yb, 23.9 at. % Co, and 71.0 at. % Sb.

B. Raman spectroscopy: Sb vibration modes

Films on all the substrates showed identical Raman spectra. Room temperature Stokes Raman spectrum of the

FIG. 1. (Color online) GIXRD patterns of the films. The XRD pattern of the target is also shown for comparison.

film is shown in Fig. 2, together with the Lorentzian fits to the experimental data. The peak positions (ν) and line widths ($\Delta\nu$) of the Lorentzian fits are displayed in Table I. The assignment of the modes was based on the Raman studies of unfilled bulk CoSb_3 by Nolas *et al.*³⁰ and the *ab initio* calculations by Rotter *et al.*¹¹ The Raman active modes are due to the relative motions of the Sb atoms and do not involve any motion of the Co sublattice even in unfilled CoSb_3 .³¹ The Sb atoms in pure CoSb_3 move with respect to one another in such a way that the center of mass of the Sb in the unit cell is fixed. The phonon frequencies obtained for the films match well with those predicted and reported for unfilled CoSb_3 ,^{11,30,34} which confirms the formation of the skutterudite phase and suggests that the dopants do not substitute for Sb, but occupy the voids in the crystal structure. The enhancement of the phonon linewidths is further proof of the filling of voids by (In, Yb). Nolas *et al.*³⁰ have observed similar increase in phonon widths in (Ge, Sn)-doped CoSb_3

FIG. 2. (Color online) Raman spectra of (In, Yb)-doped CoSb_3 film. The experimental data is shown by open circles and the overall fit by the solid black line. The individual Lorentzian line shapes are shown by the respective dashed lines. The identified phonon modes are marked.

TABLE I. Peak positions, ν and linewidths (FWHM), $\Delta\nu$ (in cm^{-1}) from Lorentzian fits to the Raman active modes for the $\text{In}_{0.1}\text{Yb}_{0.1}\text{Co}_4\text{Sb}_{12}$ film together with that reported for unfilled CoSb_3 crystallite,³⁰ the theoretically predicted zone center frequencies,¹¹ and the associated assignment of modes.

$\text{In}_{0.1}\text{Yb}_{0.1}\text{Co}_4\text{Sb}_{12}$ film ν , $\Delta\nu$	CoSb_3 crystallite ν , $\Delta\nu$	CoSb_3 theory ν
109 (F_g), 3	110 (F_g), 2	97 (F_g)
135 (E_g), 6	135 (E_g), 2	139 (E_g)
149 (A_g), 11	—	150 (A_g)
153 (F_g), 5	152 (F_g), 3	157 (F_g)
171 (F_g), 13	176 (F_g), 2	178 (F_g)
183 (A_g), 10	179 (A_g), 2	179 (A_g)
186 (E_g), 3	187 (E_g), 2	182 (E_g)

bulk, which was ascribed to the dynamic disorder produced by the dopant atoms that affect the bonding of Sb atoms that define the voids. It is clear from the broadening of the Raman active modes that In and Yb dopants rattle inside the voids of CoSb_3 and, hence, the thermal conductivity of the films must be very low compared to unfilled CoSb_3 . In fact, the films were highly susceptible to laser heating effects during Raman measurements, which further support the possible low thermal conductivity of the films.

C. Low-temperature electrical transport

In Fig. 3, we plot the electrical conductivity, from 5 to 660 K, of the films. For the whole temperature range, resistivity decreases with increase in temperature, which is typical of a semiconductor. The low-temperature semiconducting behavior is similar to what has been previously reported for CoSb_3 single crystals³⁵ and is attributed to the high quality of the thin films. The semiconducting nature of the films is strikingly in contrast with the degenerate or metallic nature of the target.¹⁷ The drastic change in the conduction mechanism of the films will be discussed later. The high-temperature electrical resistivity of the films is shown as an inset to Fig. 3 to emphasize the difference in the electrical resistivity of the films on

FIG. 3. (Color online) Temperature variation of electrical resistivity of the films. The high-temperature resistivity measured using the linear four-probe technique is shown enlarged in the inset.

FIG. 4. (Color online) $\ln(\rho)$ vs $1/T$ plot for the films. The linear fits to the high-temperature region above 250 K are also shown.

the different substrates. It can be noted that the film on Si/SiO₂ is the least resistive, whereas that on MgO is the most resistive. The reason for the difference in electrical resistivity of the films will be discussed in the next section.

From Fig. 3, it is evident that the low-temperature portion of the resistivity shows an extrinsic behavior wherein resistivity drops drastically with increase in temperature, whereas the high-temperature portion of the resistivity exhibits a behavior similar to what is expected for intrinsic semiconductors. Assuming a single-band semiconductor with parabolic density of states, the resistivity (ρ) of a semiconducting film can be expressed as

$$\rho = \frac{1}{ne\mu}, \quad (1)$$

where n is the carrier concentration, μ is the carrier mobility, and e is the elementary charge. The bandgap of the intrinsic semiconductor can be obtained from the Arrhenius relation,

$$\rho = \rho_0 \exp(\Delta/T), \quad (2)$$

where ρ_0 is the pre-exponential constant, $2\Delta = E_g$ (bandgap), and T is the absolute temperature. Hence, a plot of $\ln(\rho)$ versus $1/T$ is usually used in estimating the bandgap of semiconductors. Figure 4 shows such a plot for the data shown in Fig. 3. The linear fit in the plots was obtained in the high-temperature region, above 250 K. The bandgaps

extracted from the fits are presented in Table II. Using band-structure calculations, Singh and Pickett³⁶ have predicted a very narrow direct bandgap of 50 meV, flanked by a pseudo-gap of 0.5 eV, for undoped CoSb₃. Mandrus *et al.*³⁵ have reported the existence of the direct-gap and a pseudo-gap of 0.31 eV in high-purity single crystals of CoSb₃, closely matching the theoretical prediction. Savchuk *et al.*²⁴ have observed a pseudo-gap of 0.33 eV in CoSb₃ thin films prepared by dc magnetron sputtering. Our values for the intrinsic bandgap of the films match reasonably well with that of CoSb₃ single crystals. However, there is no evidence of an indirect bandgap in our films. The introduction of filler atoms is expected to change the band structure of CoSb₃,¹⁰ and, hence, doping of In and Yb must be the reason behind the disappearance of the pseudo-gap. From Fig. 4, it is also evident that the curves deviate from the rigid linear dependency as temperature decreases. A change from intrinsic to extrinsic conduction mechanism at low temperatures can well explain the observed deviation. The (In, Yb) dopants can introduce donor levels in the bandgap of CoSb₃, as is evident from the increase in carrier concentration observed with dopant concentration in (In, Yb)-doped bulk CoSb₃.¹⁷ Moreover, undoped single-crystalline and polycrystalline CoSb₃ exhibits *p*-type conduction, whereas bulk polycrystalline In_{0.1}Yb_{0.1}Co₄Sb₁₂ exhibits *n*-type conduction.¹⁴ As will be discussed later, we have obtained negative Seebeck and Hall coefficients indicating *n*-type conduction in all the films. Hence, the assumption that In and Yb dopants create donor levels in the bandgap of CoSb₃ can be justified. The donor levels can contribute to the conduction in the extrinsic (low-temperature) regime where the resistivity drops drastically with increase in temperature. Identifying the subtle transition region from extrinsic to intrinsic conduction with rise in temperature is difficult, however, because the In and Yb dopants are more likely to create donor bands rather than donor levels in the bandgap of CoSb₃ and, hence, the bandgap values reported in Table I are to be considered only as approximate values.

The existence of two separate conduction mechanisms in the films is further evident from the temperature variation of carrier concentration shown in Fig. 5. For all the films, carrier concentration remains almost constant in the temperature range from 5 to 250 K and increases steadily above 250 K. This should be expected if one considers the extrinsic regime below 250 K, wherein impurity band conduction is dominant and the depletion of impurity levels cannot contribute additional carriers with an increase in temperature. In

TABLE II. Calculated transport properties at 300 K of the films and that reported for the target.

Film on	Electrical resistivity (± 0.01 m Ω cm)	Bandgap (meV)	Carrier concentration ($\pm 0.01 \times 10^{20}$ cm ⁻³)	Hall mobility (± 0.1 cm ² V ⁻¹ s ⁻¹)	Seebeck coefficient (± 1 μ V K ⁻¹)	Power factor (± 0.01 W m ⁻¹ K ⁻¹)
Quartz	6.39	65	1.36	7.2	-154	0.11
MgO	7.16	47	2.69	3.2	-90	0.03
Si/SiO ₂	5.45	44	3.00	3.5	-58	0.02
Glass	6.65	64	1.19	7.9	-160	0.12
Target ^a	0.76	—	2.00	40.6	-150	0.89

^aRef. 17.

FIG. 5. (Color online) Carrier concentration of the films as a function of inverse temperature. Inset shows the calculated Hall mobility of the films as a function of temperature along with a $T^{3/2}$ fit (dotted line).

the high-temperature regime above 250 K the intrinsic conduction sets in, raising the concentration of carriers steadily. The room temperature carrier concentration of the films is comparable to that of the target (see Table II). However, the resistivity of the films is higher as compared to that of the target and is detrimental to the thermoelectric power factor. Because the films exhibit a semiconducting behavior, and the target a metallic behavior, the difference in resistivity is higher (by an order of magnitude) at 300 K and lower (roughly two times) at 660 K. The enhanced resistivity of the films is a direct result of the nanocrystalline nature of the films. The typical grain size of the films was in the range 20–50 nm (comparable to the crystallite size as determined by GIXRD), which is much smaller than that of the bulk (1–10 μ m). Hence, the number of grain boundaries per unit volume in the films is much larger compared to that of bulk. Evidently, the higher resistivity of the films stems from the enhanced scattering of carriers because of the high concentration of grain boundaries.

Because the carrier concentration of the films and the bulk are in close agreement (see Table II), the enhanced resistivity in the films implies a reduced carrier mobility. The carrier mobility of polycrystalline films is usually affected by high potential barrier for the charge carriers at the grain boundaries. The Hall mobility of our films is indeed lower compared to that of the bulk (see Table II), which is evidently because of the enhanced grain boundary scattering. It is to be noted here that different scattering mechanisms can affect the carrier mobility of the films. In the extrinsic conduction regime, the scattering is predominantly because of ionized impurities, which result in a $T^{3/2}$ dependence of carrier mobility according to the expression,

$$\mu_{\text{impurity}} \sim \frac{1}{N_i m^{*1/2}} T^{3/2}, \quad (3)$$

where T is the absolute temperature, N_i is the density of ionized impurities, and m^* is the carrier effective mass. In polycrystalline films, the grain boundary scattering influences the carrier mobility according to the relation,

$$\mu_{\text{grain}} \sim \frac{L}{T^{1/2}} e^{\left(-\frac{E_b}{k_B T}\right)}, \quad (4)$$

where L is the grain size, E_b is the average potential barrier height at the grain boundaries, and k_B is the Boltzmann constant.

From the earlier discussion on the conduction mechanisms in the films, one must expect the mobility of the films in the low-temperature region to depend on both Eqs. (3) and (4). To further validate this point, we plot the calculated Hall mobility of the films as a function of temperature in the inset to Fig. 5. The mobility of the films slowly increases as the temperature increases, suggesting scattering by ionized impurities. However, a rigid $T^{3/2}$ dependence (as indicated by the dotted lines in the inset to Fig. 5) is not observed, which implies that grain boundary scattering also is relevant at all temperatures. At temperatures above 250 K, there is marked deviation from the $T^{3/2}$ behavior indicating the onset of intrinsic conduction. The mobility tends to either saturate or slowly fall off above 300 K. In addition to the grain boundary scattering, carrier mobility in this temperature regime is most likely dependent on the acoustic-phonon scattering as per the relation,

$$\mu_{\text{acoustic}} \sim \frac{1}{m^{*5/2}} T^{-3/2}. \quad (5)$$

High-temperature mobility studies only can bring out this dependence more clearly. Nevertheless, it is clear that transport properties of the films are determined by different scattering processes at different temperature regimes.

D. High-temperature Seebeck coefficient and power factor

The temperature dependence of Seebeck coefficient of the films is shown in Fig. 6. All the films exhibit a negative Seebeck coefficient indicating n -type conduction. Undoped CoSb₃ is p -type and, hence, the n -type behavior shown by the films is a result of the doping of In and Yb. The films on glass and quartz exhibit Seebeck coefficients comparable to that of

FIG. 6. (Color online) Measured high-temperature Seebeck coefficient of the films.

FIG. 7. (Color online) Calculated power factor of the films as a function of temperature.

the bulk, whereas films on MgO and Si/SiO₂ show inferior properties (see Table II). The difference in the Seebeck coefficient of the films is in accordance with the observed electrical resistivity, Hall mobility, and carrier concentration. For instance, films on MgO and Si/SiO₂ have higher carrier concentration, lower mobility, and lower electrical resistivity compared to films on glass and quartz. Accordingly, the Seebeck coefficient of the film on MgO and Si/SiO₂ is lower. The power factor of the films as a function of temperature is plotted in Fig. 7. The films on quartz and glass exhibit a better power factor than the films on MgO and Si/SiO₂. However, because the electrical resistivity of the films is much higher than the bulk, the maximum power factor (obtained in the film on glass at 660 K) of $0.66 \text{ W m}^{-1} \text{ K}^{-1}$ is nearly four times lower than that ($2.7 \text{ W m}^{-1} \text{ K}^{-1}$) reported for the bulk.¹⁷

E. Oxygen diffusion and oxidation of CoSb₃ at the interface

The difference in the Seebeck coefficient, electrical resistivity, and, hence, the power factor of the films can be explained by considering the diffusion of oxygen across the film-substrate interface. The Co and O depth profiles for the films near the interface as measured using EELS are plotted in Fig. 8. The interface region is marked by vertical slashed lines in the plot, for each of the films. The vertical lines are drawn at the point where the Co and O core-loss signals stabilize. The thickness of the interface regions marked in the plot is 4, 9, 10, and 8 nm, respectively, for films on quartz, MgO, Si/SiO₂, and glass substrates. The diffusion of oxygen from the substrate to the films is limited to the interface region in films on quartz and glass, whereas oxygen diffuses to a much larger depth into the films (over 50 nm) on MgO and Si/SiO₂. This has been verified using EDAX depth profiling (not presented here). The difference in the oxygen diffusion profiles in the films can be explained based on the structure, density, and composition of the substrates. Though quartz and the SiO₂ overlayer of the Si/SiO₂ substrate are chemically the same, quartz is single crystalline, whereas the thermally grown SiO₂ is amorphous. The glass substrate

FIG. 8. (Color online) Co and O core-loss signal along the EELS line scan done perpendicular to the interface for the films. The x axis shows the length of the line scans in nm from which the interface region can be quantified. The interface region is marked by the vertical lines. To the left of the interface is the film and to the right, the substrate.

used in the present study is also amorphous SiO₂, but with different impurities (such as Na, B, and Ca). The diffusion of oxygen in crystalline SiO₂ is much smaller compared to that in amorphous SiO₂ mainly because of the smaller diffusion channels and larger energy barriers in crystalline SiO₂.³⁷ In glass, the impurity atoms serve to minimize the diffusion of oxygen by occupying the interstices.³⁷ Elemental Sb is reported to be the best reducing agent for MgO.³⁸ Hence, it is evident that amorphous SiO₂ and MgO substrates favor diffusion of oxygen much easier than single-crystal quartz or impurity-doped glass. The role of In and Yb in the diffusion of oxygen and any reaction processes is assumed to be negligible because of the low concentration of these dopants.

The diffusion of oxygen across the interface can occur during film deposition and post-deposition annealing. Oxidation of undoped bulk CoSb₃ exposed to air is reported to start at $\sim 644 \text{ K}$ and proceed through the formation of various intermediate oxides at high temperatures.³⁹ The highest temperature involved in the present studies is 700 K. Hence, we consider only cubic α -Sb₂O₃ (formed at $\sim 644 \text{ K}$) and β -Sb₂O₃, which in turn is oxidized to β -Sb₂O₄ (at $\sim 673 \text{ K}$), because the other intermediate oxides are formed at temperatures in excess of 773 K.³⁹ Depending upon the diffusion of oxygen from the substrate, the antimony oxides can form only in the region near the interface, because the deposition and annealing of the films were done in argon ambient. In an inert ambient, CoSb₃ decomposes into CoSb₂ and elemental Sb only at $\sim 773 \text{ K}$.⁴⁰ Hence, the formation of CoSb₂ in the bulk of the films can be ruled out. The GIXRD studies confirm the absence of any detectable CoSb₂ and oxide phases. However, near the interface region where oxygen diffusion is prominent, antimony oxides can be formed only at the expense of CoSb₃. Godlewska *et al.*⁴⁰ have put forward a multi-stage process for the oxidation of CoSb₃, involving the decomposition of CoSb₃ into CoSb₂ and Sb, and the oxidation of the product species. From the above discussion, it is reasonable to assume the presence of CoSb₂ at the regions

near the interface of the films, though it is absent in the bulk of the films. CoSb₂ is more electrically conducting and shows an inferior Seebeck coefficient as compared to CoSb₃, and high electrical conductivity and very low Seebeck coefficient have been observed in (In, Yb)-doped CoSb₃ films with CoSb₂ secondary phases.³² Hence, better electrical conductivity and lower Seebeck coefficient should be expected in films with more pronounced oxygen diffusion profile across the interface, which is indeed observed.

IV. CONCLUSION

Single-phase polycrystalline (In, Yb)-doped CoSb₃ films have been deposited on multiple substrates using PLD. The frequency of the Raman modes exhibited by the films match closely with those reported for undoped bulk CoSb₃, whereas the enhanced phonon linewidths suggest the filling of the voids by the dopant atoms. Low-temperature electrical transport studies reveal the semiconducting nature of the films with extrinsic and intrinsic conduction regimes, respectively, below and above ~250 K. The carrier concentration of the films match well with that reported for the bulk, whereas the resistivity is higher because the mobility is limited by the enhanced grain boundary scattering brought on by the high density of grain boundaries in the films. Ionized impurity scattering is dominant at low temperatures in the films, whereas acoustic-phonon scattering sets in at temperatures above 300 K. The bandgap of the films was nearly 50 meV and no pseudo-gaps were identified. Oxygen is found to diffuse more from the MgO and Si/SiO₂ substrates. The degradation of CoSb₃ at the interface into highly conducting CoSb₂ along with the oxidation of Sb, depending on the oxygen diffusion from the substrates, is proposed to be the reason behind the inferior power factor exhibited by films on MgO and Si/SiO₂ substrates. The films on glass and quartz exhibit reasonable power factors at high temperatures, though the maximum obtained value of 0.68 W m⁻¹ K⁻¹ is nearly four times lower than that reported for the bulk.

ACKNOWLEDGMENTS

H.A. acknowledges the baseline funding from KAUST and the FIC grant. S.R.S. and H.A. would like to acknowledge Professor Terry Tritt of Clemson University for providing the target.

¹G. J. Snyder and E. S. Toberer, *Nature Mater.* **7**, 105 (2008).

²C. Uher, *Semiconductors and Semimetals* (Academic, New York, 2001).

³G. S. Nolas, D. T. Morelli, and T. M. Tritt, *Annu. Rev. Mater. Sci.* **29**, 89 (1999).

⁴T. M. Tritt and M. A. Subramanian, *MRS Bull.* **31**, 188 (2006).

⁵D. Wee, B. Kozinsky, N. Marzari, and M. Fornari, *Phys. Rev. B* **81**, 045204 (2010).

⁶A. P. Grosvenor, R. G. Cavell, and A. Mar, *Phys. Rev. B* **74**, 125102 (2006).

⁷I. K. Dimitrov, M. E. Manley, S. M. Shapiro, J. Yang, W. Zhang, L. D. Chen, Q. Jie, G. Ehlers, A. Podlesnyak, J. Camacho, and Q. Li, *Phys. Rev. B* **82**, 174301 (2010).

⁸B. C. Sales, D. Mandrus, B. C. Chakoumakos, V. Keppens, and J. R. Thompson, *Phys. Rev. B* **56**, 15081 (1997).

⁹C. P. Yang, H. Wang, K. Iwasa, M. Kohgi, H. Sugawara, and H. Sato, *Appl. Phys. Lett.* **90**, 1397 (2007).

¹⁰J. Yang, L. Xi, W. Zhang, L. Chen, and J. Yang, *J. Electron. Mater.* **38**, 1397 (2009).

¹¹M. Rotter, P. Rogl, A. Grytsiv, W. Wolf, M. Krisch, and A. Mirone, *Phys. Rev. B* **77**, 144301 (2008).

¹²G. A. Slack, *CRC Handbook of Thermoelectrics* (CRC, Boca Raton, 1995).

¹³C. B. Vining, *Nature Mater.* **7**, 765 (2008).

¹⁴J. Y. Peng, P. N. Alboni, J. He, B. Zhang, Z. Su, T. Holgate, N. Gothard, and T. M. Tritt, *J. Appl. Phys.* **104**, 053710 (2008).

¹⁵W. Y. Zhao, C. L. Dong, P. Wei, W. Guan, L. S. Liu, P. C. Zhai, X. F. Tang, and Q. J. Zhang, *J. Appl. Phys.* **102**, 113708 (2007).

¹⁶Y. Wang, X. Xu, and J. Yang, *Phys. Rev. Lett.* **102**, 175508 (2009).

¹⁷J. Y. Peng, J. He, Z. Su, P. N. Alboni, S. Zhu, and T. M. Tritt, *J. Appl. Phys.* **105**, 084907 (2009).

¹⁸J. Y. Peng, J. He, P. N. Alboni, and T. M. Tritt, *J. Electron. Mater.* **38**, 981 (2009).

¹⁹D. W. Song, W. L. Liu, T. Zeng, T. Borca-Tasciuc, G. Chen, J. C. Caylor, and T. D. Sands, *Appl. Phys. Lett.* **77**, 3854 (2000).

²⁰H. A. Durand, K. Nishimoto, K. Ito, and I. Kataoka, *Appl. Surf. Sci.* **154**, 387 (2000).

²¹J. C. Caylor, M. S. Sander, A. M. Stacy, J. S. Harper, R. Gronsky, and T. Sands, *J. Mater. Res.* **16**, 2467 (2001).

²²J. C. Caylor, A. M. Stacy, R. Gronsky, and T. Sands, *J. Appl. Phys.* **89**, 3508 (2001).

²³V. Savchuk, J. Schumann, B. Schupp, G. Behr, N. Mattern, and D. Souptel, *J. Alloys Compd.* **351**, 248 (2003).

²⁴V. Savchuk, A. Boulouz, S. Chakraborty, J. Schumann, and H. Vinzelberg, *J. Appl. Phys.* **92**, 5319 (2002).

²⁵B. Schupp, I. Bacher, M. Hecker, N. Mattern, V. Savchuk, and J. Schumann, *Thin Solid Films* **434**, 75 (2003).

²⁶A. L. E. Smalley, S. Kim, and D. C. Johnson, *Chem. Mater.* **15**, 3847 (2003).

²⁷R. Zeipl, J. Walachová, J. Lorinčík, S. Leshkov, M. Josieková, M. Jelínek, T. Kocourek, K. Jurek, J. Navrátil, L. Beneš, and T. Plecháček, *J. Vac. Sci. Technol. A* **28**, 523 (2010).

²⁸D. Colceag, A. Dauscher, B. Lenoir, V. Da Ros, R. Birjega, A. Moldovan, and M. Dinescu, *Appl. Surf. Sci.* **253**, 8097 (2007).

²⁹G. S. Nolas and C. A. Kendziora, *Phys. Rev. B* **59**, 6189 (1999).

³⁰G. S. Nolas, C. A. Kendziora, and H. Takizawa, *J. Appl. Phys.* **94**, 7440 (2003).

³¹G. S. Nolas, G. A. Slack, T. Caillat, and G. P. Meisner, *J. Appl. Phys.* **79**, 2622 (1996).

³²S. R. Sarath Kumar, A. Alyamani, J. W. Graff, T. M. Tritt, and H. N. Alshareef, *J. Mater. Res.* **26**, 1836 (2011).

³³A. Zhou, L. Liu, P. Zhai, W. Zhao, and Q. Zhang, *J. Appl. Phys.* **109**, 113723 (2011).

³⁴J. L. Feldman and D. J. Singh, *Phys. Rev. B* **53**, 6273 (1996).

³⁵D. Mandrus, A. Migliori, T. W. Darling, M. F. Hundley, E. J. Peterson, and J. D. Thompson, *Phys. Rev. B* **52**, 4926 (1995).

³⁶D. J. Singh and W. E. Pickett, *Phys. Rev. B* **50**, 11235 (1994).

³⁷M. A. Lamkin, F. L. Riley, and R. J. Fordham, *J. Eur. Ceram. Soc.* **10**, 347 (1992).

³⁸C. A. Eckert, R. B. Irwin, and C. W. Graves, *I&EC Process Des. Dev.* **23**, 210 (1984).

³⁹J. Leszczynski, K. Wojciechowski, and A. Malecki, *J. Therm. Anal. Calorim.* **105**, 211 (2011).

⁴⁰E. Godlewska, K. Zawadzka, A. Adamczyk, M. Mitoraj, and K. Mars, *Oxid. Met.* **74**, 113 (2010).