

Structural and thermoelectrical characterization of epitaxial Sb₂Te₃ high quality thin films grown by thermal evaporation.

Georg Bendt¹, Kevin Kaiser¹, Alla Heckel¹, Felix Rieger², Dennis Oing³, Axel Lorke³, Nicolas Perez Rodriguez⁴, Gabi Schierning⁴, Christian Jooss² and Stephan Schulz^{1*}

¹Faculty of Chemistry, Inorganic Chemistry, and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Universitätsstr. 7, 45114 Essen, Germany

²Institute of Material Physics, University of Göttingen, 37077 Göttingen, Germany

³Faculty of Physics and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Lotharstraße 1, 47048 Duisburg, Germany

⁴Institute for Metallic Materials, Leibniz Institute for Solid State and Materials Research Dresden (IFW Dresden), Helmholtzstr. 20, 01069 Dresden, Germany

Abstract

Thermal evaporation of Sb₂Te₃ powder was systematically studied under various pressure and temperature conditions. Low pressure experiments (5·10⁻⁶ mbar) conducted inside a horizontal tube reactor at a temperature range of 500 - 600 °C generated rough polycrystalline films on Si(100) substrates. Based on these experiments, the chemical composition of the resulting films the furnace temperature. Enhancing the reactor pressure to 20 mbar shifted the growth zone towards higher temperature ranges and yielded highly *c*-oriented Sb₂Te₃ films on Si(100) and Al₂O₃(0001) substrates. Additional experiments were conducted inside a special reactor containing two independent heaters to study the effects of the evaporator and substrate temperatures independently. In contrast to the samples generated in the previous reactor, a two-zone heating reactor allowed the growth of epitaxial Sb₂Te₃ films with a very smooth surface topology on Al₂O₃(0001) substrates, as shown by SEM, EDX, XPS, and HRTEM. The electrical *in-plane* conductivity of the Sb₂Te₃ films decreased with increasing temperature, ultimately reaching 3950 S·cm⁻¹ at 300 K. The films showed a *p*-type carrier concentration of 4.3·10⁻¹⁹ cm⁻³ at 300 K and a very high carrier mobility of 558 cm²·V⁻¹·s⁻¹. The Seebeck coefficient increased monotonically from 94 μV·K⁻¹ at 270 K to 127 μV·K⁻¹ at 420 K.

1. Introduction

Since the early studies of Werner Haken in 1910, binary tetradymite-type materials such as Sb₂Te₃ and Bi₂Te₃ remain amongst the most studied thermoelectric materials until today.[1] These binary materials as well as their solid ternary solutions (Sb_xBi_{1-x})₂Te₃ show excellent thermoelectric performance near room temperature (< 300 °C).[2] On the other hand, topological insulators are a class of materials that exhibit an insulating bulk state and a topologically protected metallic surface state with a Dirac-like band structure. [3-8] Interestingly, high-quality *c*-oriented epitaxial Sb₂Te₃ thin films have been extensively investigated over the last decade due to their promising potential to serve as thermoelectric or topological insulating materials in various fields of technical applications. Despite the growing interest for these materials, complex anisotropic crystal structures (space group R $\bar{3}m$ (#166)) often favor the formation of rough surface morphologies, thus hampering the formation of high-quality epitaxial films. In addition, high deposition temperatures which are generally required to achieve a high surface mobility of the adatoms typically give Te deficient materials. Consequently, Te lattice sites are replaced by Sb anti-site defects, which ultimately influences the electronic properties of the resulting film.



This work may be used under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 License (CC BY-NC-ND 4.0)

Several deposition techniques including physical and chemical deposition methods, were applied in the growth of epitaxial tetradymite-type thin films. However, a more detailed analysis demonstrated that *metal organic chemical vapor deposition* (MOCVD) and *molecular beam epitaxy* (MBE) are the only processes suitable for the deposition of highly stoichiometric epitaxial tetradymite films with very smooth surface areas.[9-11] Unfortunately, both deposition techniques demand high requirements on the experimental setup and vacuum conditions. Long deposition times, relatively small-sized substrates (MBE), toxicity and air/moisture sensitivity of the likely used metal organic precursors (MOCVD) are additional drawbacks. In contrast, *physical vapor deposition* (PVD) in which purified material powders are evaporated and subsequently deposited on a given substrate, proved to be a better alternative for thin film deposition. Due to the simplicity and industrial scalability of PVD, several authors have investigated the deposition of Sb_2Te_3 films either by thermal co-evaporation of elemental Sb and Te powders or by thermal evaporation of Sb_2Te_3 powder. In fact, PVD processes were also applied for the growth of ternary solid solutions such as $(\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3$ and $\text{Bi}_2(\text{Te}_x\text{Se}_{1-x})_3$. [16-19] Goncalves et al. reported on the growth of polycrystalline Sb_2Te_3 films on polyimide and glass substrates at substrate temperatures ranging from 150 - 200 °C; the resulting films showed high Seebeck coefficients of up to $190 \mu\text{V}\cdot\text{K}^{-1}$. [12] The same group later reported on the growth of *n*-type Bi_2Te_3 films on glass, silicon, and polyimide substrates by thermal co-evaporation of Bi and Te powder at a low pressure of $5\cdot 10^{-6}$ mbar. [13] Lin et al. have successfully grown Sb_2Te_3 films on SiO_2 substrates at low substrate temperatures ($T_{\text{Sub}} = 50 - 150$ °C) which showed a Seebeck coefficient of up to $112 \mu\text{V}\cdot\text{K}^{-1}$ and a power factor of $3.94 \mu\text{V}\cdot\text{cm}^{-1}\cdot\text{K}^{-2}$. [14, 15] However, the films were found to contain elemental tellurium of which the concentration was strongly dependent of the substrate temperature; the tellurium concentration decreased with increasing temperature.

The thermal (co-)evaporation of tetradymite films is usually performed under high vacuum conditions, while the resulting films are typically grown at low substrate temperatures ($T < 200$ °C). Unfortunately, the resulting films are often amorphous or nanocrystalline, and can exhibit high electrical resistivity which make an additional annealing step necessary. It is noteworthy that high substrate temperatures are beneficial for the quality of the film. For example, Zou et al. have grown Sb_2Te_3 films by thermal co-evaporation on glass substrates at 150, 230 and 260 °C substrate temperatures. Films deposited at $T_{\text{Sub}} = 260$ °C showed the highest Seebeck coefficient ($165 \mu\text{V}\cdot\text{K}^{-1}$) and a low electrical resistivity of $1.14 \text{ m}\Omega\cdot\text{cm}$ [20]. Comparable findings were reported by Huang et al. for Sb_2Te_3 films which were grown by co-evaporation methods on SiO_2 substrates at a substrate temperature of 230 °C and a working pressure of 10^{-6} mbar. The films showed a high degree order on *c*-orientation, but displayed a very rough surface morphology due to the formation of freestanding Sb_2Te_3 hexagons. [21]

To the best of our knowledge, the growth of epitaxial tetradymite-type material films with a smooth and homogeneous substrate morphology has not been reported to date. Herein however, we report on the growth of high-quality Sb_2Te_3 films by thermal evaporation of Sb_2Te_3 powder and systematic investigations on the influence of the deposition parameters including pressure conditions, evaporation and deposition temperature, substrate material and reactor design. In addition, the transport properties of epitaxial Sb_2Te_3 films were determined.

2. Experimental Section

General. Sb_2Te_3 (99.999 %) powder was commercially available (abcr) and used as received. Si(100) and Al_2O_3 (0001) substrates were obtained from Crystec.

Reactor I. Initial experiments were carried out in a horizontal quartz tube reactor (Fig. 1) at a working pressure of $5\cdot 10^{-6}$ mbar and evaporation/deposition time of 30 minutes. The temperature of the furnace

was raised to the evaporation temperature ($T_{\text{evap}} = 500 - 600 \text{ }^{\circ}\text{C}$) and halted for 1 h. Upon reaching isothermal conditions, the powder sample holder (molybdenum boat) containing Sb_2Te_3 powder was magnetically transferred to the center of the furnace. Si(100) substrates ($10 \text{ mm} \cdot 50 \text{ mm}$) were placed next to the Sb_2Te_3 powder in the temperature gradient at the tube outlet. After 30 minutes of film deposition, the system furnace was cooled to ambient temperature within 30 minutes under vacuum.

Reactor II. Sb_2Te_3 thin films were grown within 15 minutes on $\text{Al}_2\text{O}_3(0001)$ substrates in a vertical reactor (Fig. 1) at a 20 mbar reactor pressure, which was established by a membrane pump. The Sb_2Te_3 powder and the substrate were heated independently. The evaporator temperature was varied from 540 - 620 $^{\circ}\text{C}$ and the substrate temperature was varied from 300 - 400 $^{\circ}\text{C}$. After 15 minutes of film deposition, the furnace was cooled to ambient temperature within 30 minutes under vacuum.

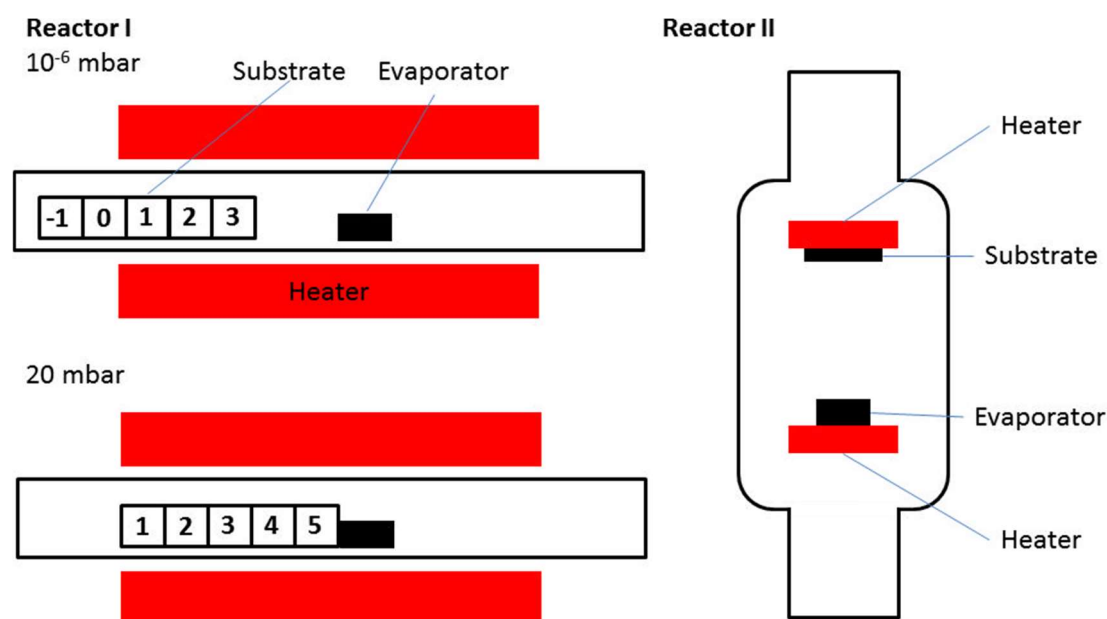


Figure 1: Schematic representation of **reactor I** (hot-wall reactor) and **reactor II** (cold-wall reactor). Note the different substrate position in **reactor I** depending on the reactor pressure.

X-ray analysis. XRD patterns were obtained using a Bruker D8 Advance powder diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$).

X-ray photoelectron spectroscopy. XPS studies were performed using a Versaprobe IITM (UlvacPhi) with monochromatic $\text{Al K}\alpha$ light at 1486.6 eV photon energy. For depth-profiling this machine is equipped with an Ar-sputter source. The emission angle between analyzer and sample is 45° .

HRTEM analysis. TEM lamellas have been prepared using a Nova Nanolab 600 (FEI) Focused Ion Beam system. Most FIB preparation steps have been done at 30 kV acceleration voltage. Due to the high beam sensitivity of the van der Waals bonded Sb_2Te_3 films, the last thinning steps were performed at 5 kV, only. This gives thin TEM lamellas with minimized surface damage and suitable for HRTEM. The HRTEM studies were performed using an image C_s corrected Titan 80-300 (FEI), lateral resolution limit 0.85 \AA , at 300 kV acceleration voltage.

Transport measurements. The Hall coefficient was measured in magnetic fields ranging between -2 T and 2 T, in a temperature range of 7.5 to 300 K, using a closed cycle cryostat. The carrier concentration n was calculated by $n = 1/e \cdot R_H$, where R_H is the Hall coefficient. The Conductivity σ was measured in 4-point geometry. The carrier mobility μ was calculated by $\mu = \sigma \cdot R_H$. The Seebeck

coefficient from 240 to 420 K was measured on a Linseis LSR-3 system. The Seebeck coefficient in cross-plane geometry was characterized using a potential Seebeck microprobe from Panco GmbH.

3. Results and discussion

Reactor I. Commercial Sb_2Te_3 powder was evaporated in the center of a quartz tube placed in a horizontal tube furnace. The reactor temperature was varied from $T_{\text{evap}} = 500 - 600$ °C, while the reactor pressure was kept constant at $5 \cdot 10^{-6}$ mbar. Si(100) substrates (50 mm · 10 mm) were divided into 10 mm by 10 mm sections (Fig. 1). Due to the temperature gradient between the heating zone and the outlet of the furnace, the substrate temperature ranged from 70 °C (section -1) to 225 °C (section 3). The evaporation rate of Sb_2Te_3 was found to be strongly dependent of the reactor temperature. Figure 2 shows the SEM photographs of different substrate sections of a material film that was deposited at $T_{\text{evap}} = 600$ °C (these photographs are displayed in larger size in the electronic supplement). Sections at low substrate temperatures T_{sub} (sections -1, 0) show a rough surface morphology consisting of 500 nm thick hexagons. These structures consist of stacks of thinner hexagons that grew tilted on the substrate surface. The hexagon stacks become thinner and more defined at moderate substrate temperatures (sections 1, 2). In contrast, films grown at higher substrate temperatures (section 3) consist of hexagons that are preferentially grown *c*-oriented on the substrate.

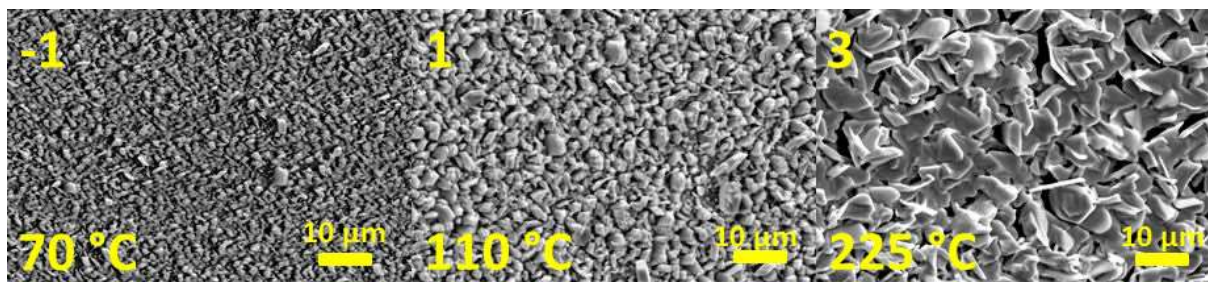


Figure 2. SEM photographs of different sections of material films grown on Si(100) substrates at $T_{\text{evap}} = 600$ °C in reactor I at $5 \cdot 10^{-6}$ mbar.

The EDX analysis of the as-deposited Sb_2Te_3 films shows a strong influence of the evaporation temperature T_{evap} , but only a weak influence of the substrate temperature. At high T_{evap} (550 °C, 600 °C), the Sb_2Te_3 powder was completely evaporated and the film composition was found to be Te-deficient. At a lower T_{evap} of 500 °C, only 40 mg of the Sb_2Te_3 powder was evaporated, but a film with a nearly stoichiometric Sb to Te ratio of 2:3 was obtained.

Table 1. Sb:Te [at-%] molar ratio of Sb_2Te_3 films grown on Si(100) (section -1 to 3) at $T_{\text{evap}} = 500, 550$ and 600 °C in reactor I at $5 \cdot 10^{-6}$ mbar as determined by EDX analysis.

T_{evap} [°C]	Section -1	Section 0	Section 1	Section 3	Section 3
600	46.9 : 53.1	46.3 : 53.7	46.4 : 53.6	46.3 : 53.7	43.1 : 56.9
550	38.7 : 61.3	38.8 : 61.2	38.7 : 61.7	38.7 : 61.3	38.6 : 61.4
500	41.2 : 58.8	40.1 : 59.9	39.4 : 60.6	40.2 : 59.8	41.2 : 58.8

The XRD patterns for the Sb_2Te_3 film grown on sections -1 to 3 at different T_{evap} are displayed in figure 3. For all samples, the presence of rhombohedral Sb_2Te_3 was confirmed by comparison with the reported peak positions (PDF 15-874). The film deposited at $T_{\text{evap}} = 500$ °C contained small amounts of elemental Te (PDF 36-1452) as secondary phase as determined by XRD. In general, the films were strongly textured and became more *c*-oriented with increasing T_{evap} and T_{sub} . The intensity ratio between the 006 reflection at $2\Theta = 26.3^\circ$ and the 015 reflection $2\Theta = 28.3^\circ$ was used to estimate the degree of *c*-orientation. At $T_{\text{evap}} = 600$ °C, the 015 reflection was almost fully suppressed and the

reflections corresponding to the 001 crystal planes ($l = 3, 6, 9, 12 \dots$) were strongly pronounced, indicating a high degree of c -orientation.

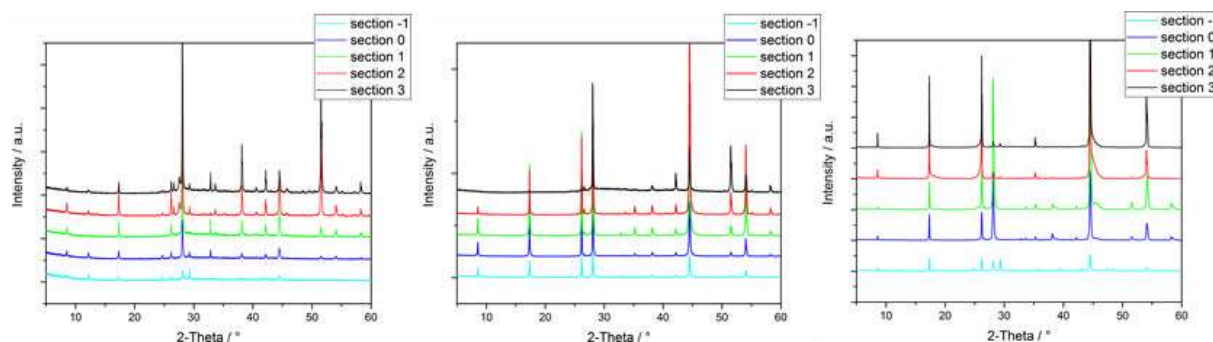


Figure 3. X-ray diffractograms of Sb_2Te_3 films grown on Si(100) (sections -1 ... 3) at $T_{\text{evap}} = 500$ °C (left), 550 °C (middle) and 600 °C (right); **reactor I**, $5 \cdot 10^{-6}$ mbar.

The growth of Sb_2Te_3 films was then investigated at a working pressure of 20 mbar and the Sb_2Te_3 powder was evaporated at 600 °C. The change of the pressure conditions from $5 \cdot 10^{-6}$ mbar to 20 mbar not only shifted the growth zone of the Sb_2Te_3 films towards higher substrate temperatures compared to the experiments at $5 \cdot 10^{-6}$ mbar, but also resulted in the growth of several micrometer large Te crystals in addition to very thin Sb_2Te_3 plates on the cold end of the substrate (sections 1, 2). In contrast, pure Sb_2Te_3 plates were grown at higher substrate temperatures (section 3). The thickness of the Sb_2Te_3 plates increased with increasing substrate temperature, finally resulting in thin films at 370 °C (section 5) as shown in figure 4. The Sb_2Te_3 plates grew highly c -oriented with respect to the substrate surface, but very few freestanding discs were present. The elemental composition of the Sb_2Te_3 flakes were determined by EDX analysis. Regardless of the substrate position, Sb:Te ratios close to the ideal composition of 40:60 at% were found.

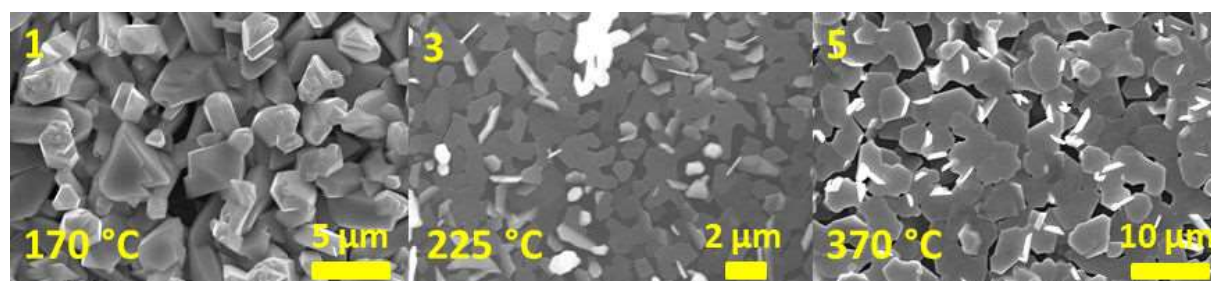


Figure 4. SEM photographs of Sb_2Te_3 films grown on Si(100) substrates at different substrate sections (**reactor I**, 20 mbar).

To investigate the influence of the substrate material on the morphology and chemical composition of the resulting Sb_2Te_3 films, we further investigated the growth on $\text{Al}_2\text{O}_3(0001)$ substrates. SEM photographs (Fig. 5) of the resulting films reveal the growth of exclusively c -oriented Sb_2Te_3 flakes on the substrate, which already starts at moderate substrate temperatures (section 3), whereas vertical and agglomerated discs are formed at lower substrate temperatures (sections 1, 2). With increasing substrate temperature, the flakes were found to coalesce into closed and smooth Sb_2Te_3 films (sections 4, 5). The EDX analysis of as-formed films proved the formation of stoichiometric Sb_2Te_3 films on sections 3 - 5.

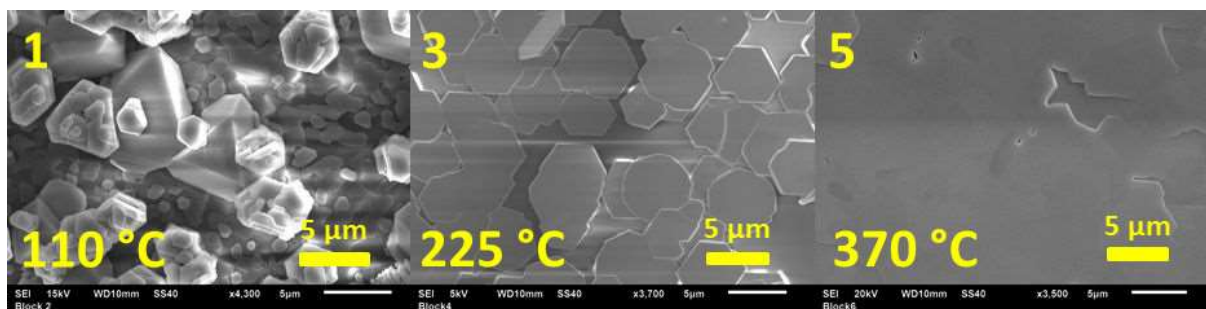


Figure 5. SEM photographs of Sb_2Te_3 films grown on $\text{Al}_2\text{O}_3(0001)$ substrates at different substrate temperatures (**reactor I**, 20 mbar).

The growth of highly c -oriented Sb_2Te_3 films is supported by the XRD analysis (Fig. 6). Starting with section 3, only reflections corresponding to the 001 ($l=3, 6, 9, 12 \dots$) lattice planes of phase-pure Sb_2Te_3 were observed. The presence of any additional second crystalline phase, including Sb , Sb_2O_3 , Te and TeO_2 , can be excluded.

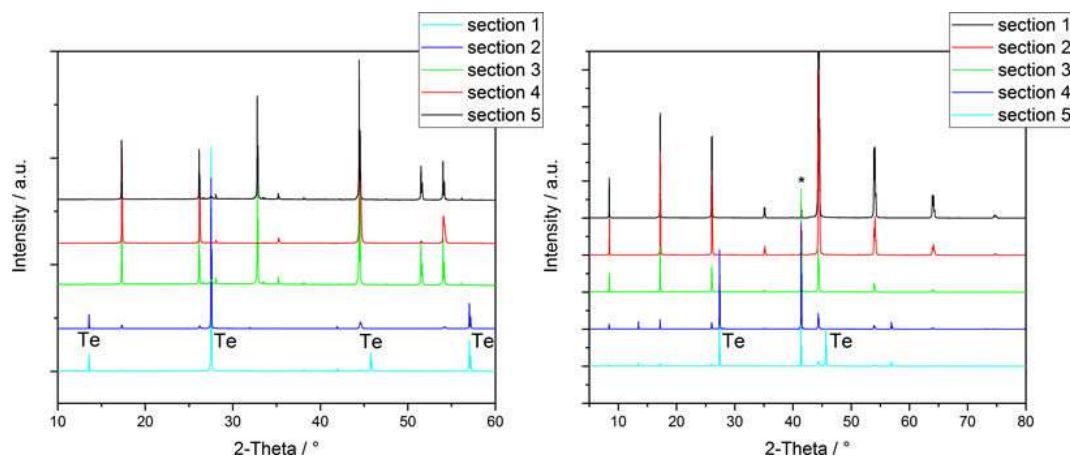


Figure 6. X-ray diffractogram of Sb_2Te_3 films grown on $\text{Si}(100)$ (left) and $\text{Al}_2\text{O}_3(0001)$ (right) substrates on different substrate sections in **reactor I** at 20 mbar.

The deposition experiments on $\text{Si}(100)$ substrates in **reactor I** showed that the reactor pressure plays an important role in the deposition of high quality Sb_2Te_3 films. The films grown at low pressure conditions ($5 \cdot 10^{-6}$ mbar) are dense and do not show any tendency towards the formation of holes, but rather show rough surface morphologies. In contrast, high pressure conditions (20 mbar) resulted in high deposition rates, but the as-formed films are non-stoichiometric and contain secondary phases of elemental Sb and/or Te . In addition, increasing the reactor pressure from $5 \cdot 10^{-6}$ mbar to 20 mbar shifted the growth zone towards higher substrate temperatures. The resulting Sb_2Te_3 films show a strong c -orientation and exhibit a nearly stoichiometric chemical composition ($\text{Sb}:\text{Te}$ molar ratio of 2:3). Clearly, the evaporation of Te from the as-deposited film is suppressed under these high-pressure conditions (20 mbar). Moreover, the substrate material also plays vital role in the growth of high-quality epitaxial Sb_2Te_3 films. While highly textured Sb_2Te_3 films were grown on $\text{Si}(100)$, most likely due to the presence of a thin (amorphous) silicon oxide layer, epitaxial Sb_2Te_3 films were obtained on $c\text{-Al}_2\text{O}_3(0001)$ ($c\text{-Al}_2\text{O}_3$) substrates instead. In contrast, PVD growth experiments of Sb_2Te_3 films on Al_2O_3 substrates with different orientation (11-20 (A) and 1-100 (M)) did not yield epitaxial films (electronic supplement).

To investigate the growth of high-quality Sb_2Te_3 films in more detail and to gain a better control over the growth conditions, we modified the reactor geometry. In this case, a cold-wall reactor with an

independently heated sample holder and substrate holder was developed to favor the growth of large and homogeneous Sb_2Te_3 films.

Reactor II. A cold-wall reactor for the deposition of smooth epitaxial Sb_2Te_3 films on $\text{Al}_2\text{O}_3(0001)$ substrates was developed (Fig. 1). Its design was based on the initial experiments in the horizontal tube reactor. In contrast to the tube reactor, the use of independent heaters for the substrate and the evaporator allows for a more precise control over the deposition conditions such as the substrate and evaporation temperatures, as well as the resulting growth rate. Optimal conditions for the deposition of Sb_2Te_3 films were found by systematic variations of the substrate and the evaporator temperatures. All experiments were performed at a reactor pressure of 20 mbar. The evaporator temperature in the first deposition series was fixed to 580 °C and the substrate temperature was varied between 300 °C and 400 °C. Dense films were grown at 300 °C, which showed a rather rough surface morphology due to the formation of isolated Sb_2Te_3 columns. Increasing the substrate temperature to 325 °C resulted in the reduction of columnar structures, while a further increase of the substrate temperature to 350 °C resulted in the growth of very smooth and continuous Sb_2Te_3 films. In contrast, substrate temperatures of 375 and 400 °C resulted in the growth of isolated hexagons instead of continuous Sb_2Te_3 films, likely due to higher desorption rates from the substrate surface (Fig. 7).

In a second deposition series, the substrate temperature was fixed to 350 °C and the evaporator temperature was varied between 540 to 620 °C. At a low evaporator temperature of 540 °C, the deposited film exhibited several holes. This behavior strongly indicates an insufficient supply of material flux. Dense and smooth films were obtained at 560 and 580 °C, whereas rough films were obtained at even higher temperatures due to a higher precursor flux reaching the substrate.

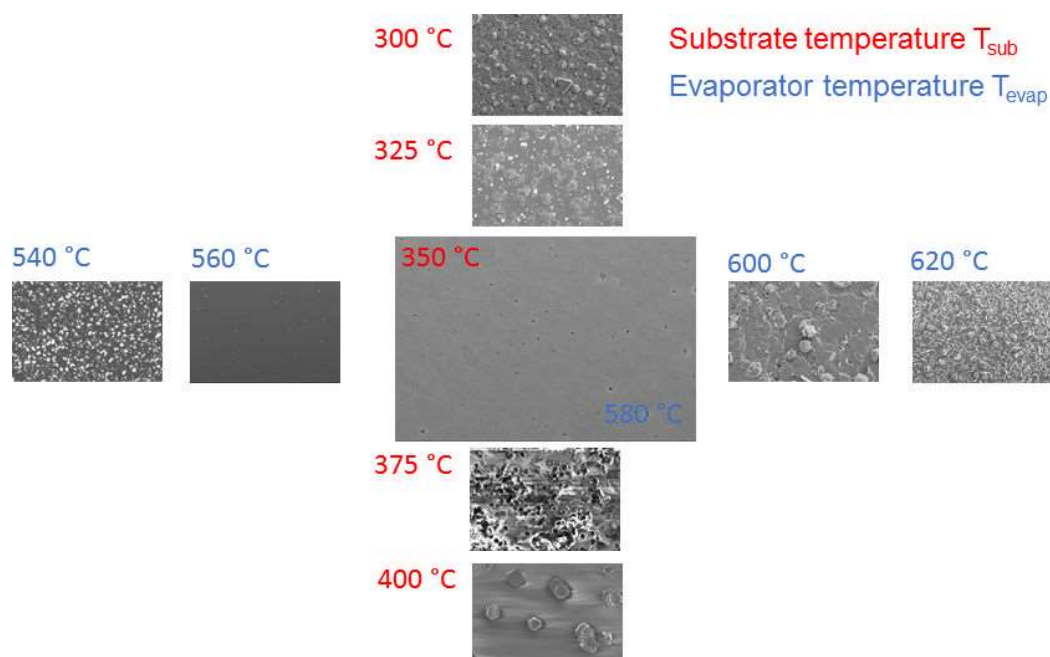


Figure 7. SEM photographs of Sb_2Te_3 films grown on $\text{Al}_2\text{O}_3(0001)$ substrates at different substrate and evaporator temperatures grown in **reactor II** at 20 mbar.

The XRD pattern of a Sb_2Te_3 film grown at 350 °C on an $\text{Al}_2\text{O}_3(0001)$ substrate in **reactor II** is shown in figure 8. All Bragg reflections with a significant intensity can be indexed on the basis of the structure of rhombohedral Sb_2Te_3 . There is no indication for the formation of elemental Sb or Te as well as the corresponding oxides (Sb_2O_3 , TeO_2). The XRD pattern shows the characteristic $00l$ ($l = 3, 6, 9, 12 \dots$) reflections for c -orientated Sb_2Te_3 (PDF 15-874).

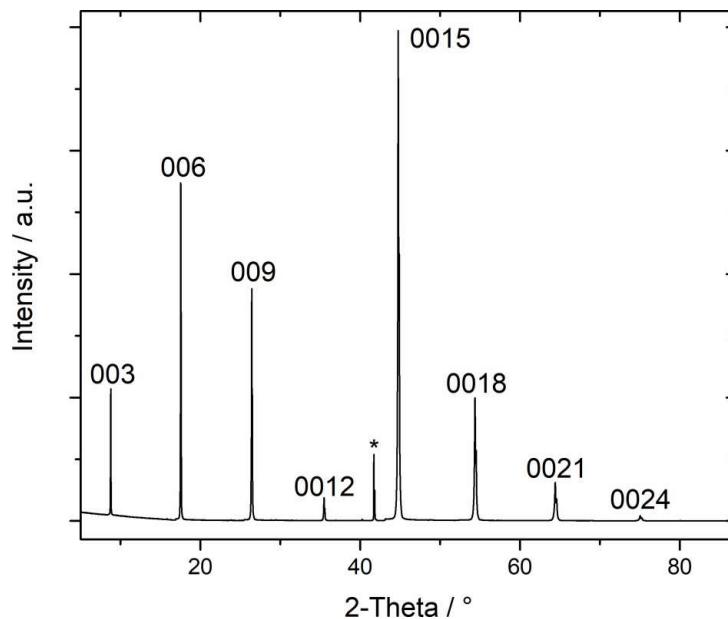


Figure 8. X-ray diffractogram of a Sb_2Te_3 film grown at 350 °C on a $\text{Al}_2\text{O}_3(0001)$ substrate grown in **reactor II**.

The X-ray photoelectron spectrum (XPS) of a Sb_2Te_3 film grown on an $\text{Al}_2\text{O}_3(0001)$ substrate at 350 °C (figure 9) shows strong peaks for Sb $3d_{3/2}$ and $3d_{5/2}$ at 539 and 529 eV and Te $3d_{3/2}$ and $3d_{5/2}$ at 582.9 and 572.5 eV, respectively. These values are in good agreement with reported binding energies of Sb and Te oxide species, indicating that the film surface is covered with a thin layer of $\text{Sb}_2\text{Te}_3\text{-O}_x$ that is either amorphous or too thin to be detected by XRD. In addition, a second set of weak peaks at lower binding energies is visible for the elements corresponding to metallic antimony and tellurium in Sb_2Te_3 . An angle-dependent measurement was used to calculate the thickness of the oxidized surface layer. The XPS study shows a partially oxidized surface of 3.2 ± 1.1 nm thickness.[22]

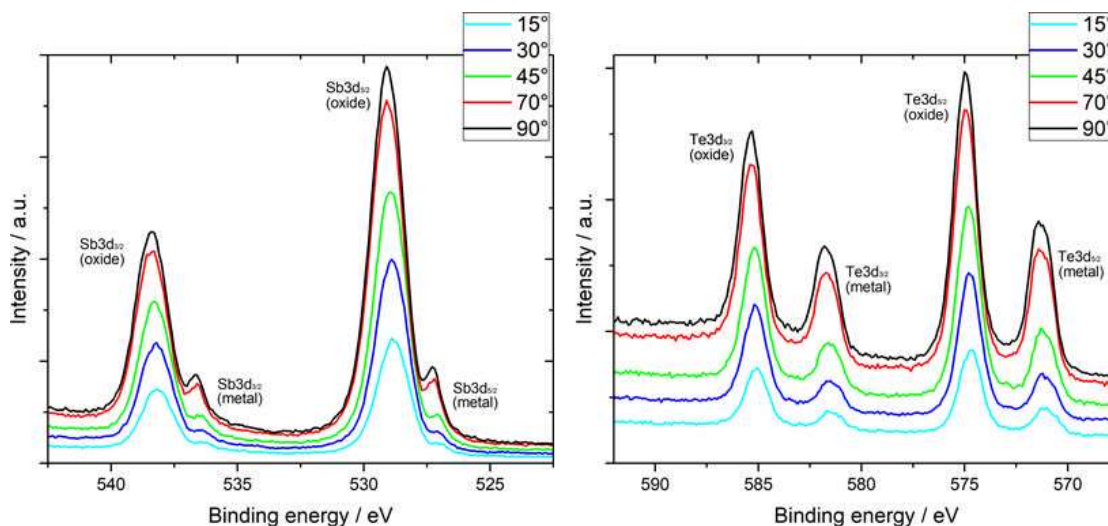


Figure 9. XPS core level Sb (left) and Te (right) spectra of a Sb_2Te_3 film grown at 350 °C on a $\text{Al}_2\text{O}_3(0001)$ substrate.

A TEM lamella of a Sb_2Te_3 film was prepared by the focused ion beam technique to investigate the film-substrate interface by HRTEM in more details. The FFT pattern is shown as inset in figure 10A. The growth of the Sb_2Te_3 film starts with one or two quintuple layers, which are rather largely disordered according to the HRTEM study. The disorder at the interface between the Al_2O_3 substrate and the growing Sb_2Te_3 film most likely results from the partial oxidation of the first Sb_2Te_3

layers.[25] Thereafter, highly crystalline quintuple layers of Sb_2Te_3 are epitaxially grown, and show very low number of stacking faults.

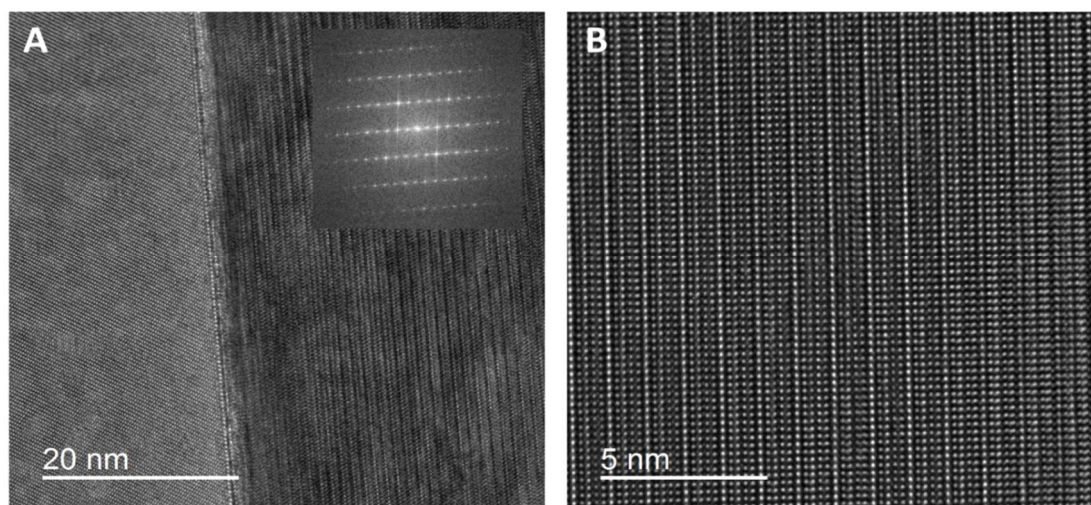


Figure 10. HRTEM image of the substrate film interface of a 500 nm thick Sb_2Te_3 film including a FFT of the film as inset, showing 001 growth (A). HRTEM image of a sectioned area in a 200 nm thick Sb_2Te_3 film with higher magnification, revealing high crystallinity and highly regular growth (B). Both films are grown at 333 °C on an $\text{Al}_2\text{O}_3(0001)$ substrate.

The temperature dependence of *in-plane* transport properties such as the carrier concentration n , the carrier mobility μ , and the conductivity σ of epitaxial PVD Sb_2Te_3 films grown at 350 °C on $\text{Al}_2\text{O}_3(0001)$ was determined by a combined conductivity and Hall effect measurement. In figure 11A, the electrical conductivity of the Sb_2Te_3 film as a function of the temperature is displayed. The film shows a metallic behavior and a monotonic decrease of the electrical conductivity with increasing temperature as was previously observed for MOCVD-grown epitaxial Sb_2Te_3 thin films.[10] At 300 K an electrical conductivity of $3950 \text{ S}\cdot\text{cm}^{-1}$ was measured. The film showed a high *p*-type carrier concentration (Fig. 11C) of $7.5\cdot 10^{19} \text{ cm}^{-3}$ which remained nearly constant for temperatures $T < 100 \text{ K}$, and then decreases with increasing temperature to $4.3\cdot 10^{19} \text{ cm}^{-3}$ at 300 K. In consistence with the observed metallic behavior, the carrier mobility (Fig. 11B) decreases with increasing temperature reaching $558 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ at 300 K. Remarkably, the carrier mobility is even higher than the value reported for single crystals ($365 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$).[27] Comparable high values are only found for epitaxial or highly textured Sb_2Te_3 films. For example, a carrier mobility of $330 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ was reported for MOCVD grown films,[22] $303 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ for thermal co-evaporated films,[20] and $433 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ for Sb_2Te_3 films prepared by nano-alloying,[23] whereas lower values were reported for polycrystalline Sb_2Te_3 samples prepared by thermal evaporation in high vacuum.[24] Figure 11D shows the Seebeck coefficient and the power factor values of a Sb_2Te_3 film with respect to temperature (240 - 420 K). The Seebeck coefficient monotonically increases in the temperature region from $94 \mu\text{V}\cdot\text{K}^{-1}$ at 270 K to $127 \mu\text{V}\cdot\text{K}^{-1}$ at 420 K. Based on the electrical conductivity and the Seebeck coefficient, a power factor of $33 \mu\text{W}\cdot\text{cm}^{-1}\cdot\text{K}^{-2}$ was calculated. The cross-plane Seebeck characterization at room temperature (Fig. 11 E) showed good overall homogeneity and a Seebeck coefficient of $113 \mu\text{V} \pm 6 \mu\text{V}$ in the scanned area of 4 mm x 4 mm. We recently reported on *cross-plane* measurements of the thermal conductivity of epitaxial Sb_2Te_3 films using the 3-omega method. At 300 K, a very low thermal conductivity of $1.6 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ was observed.[25]

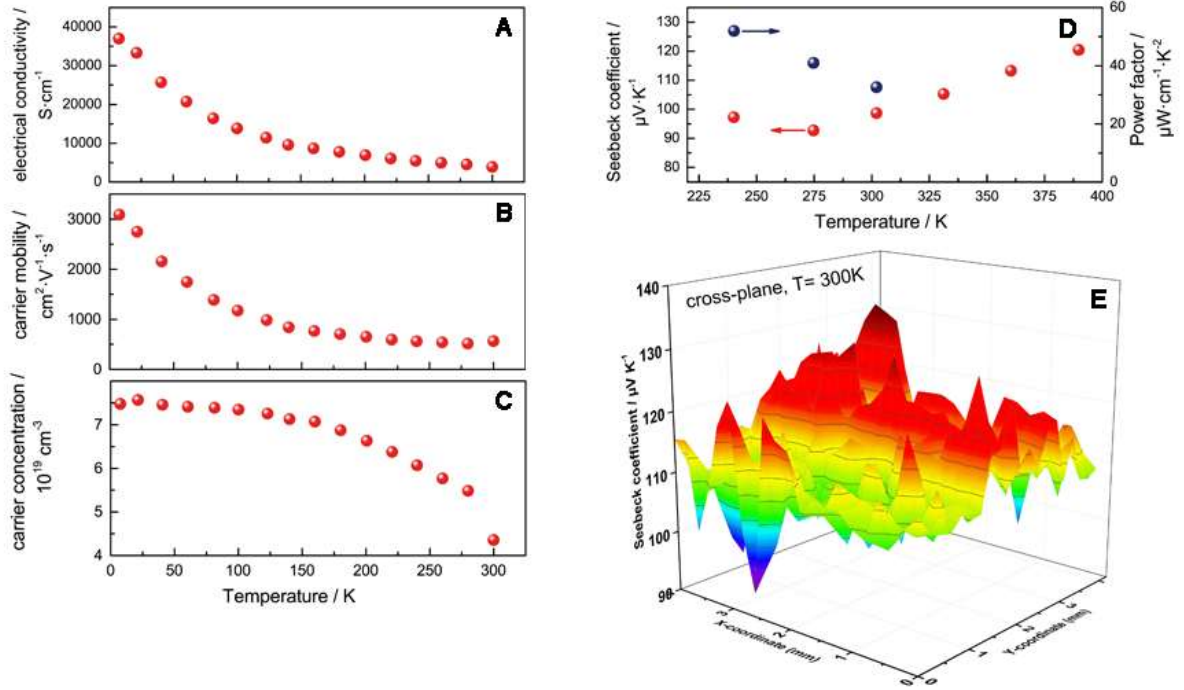


Figure 11. Electrical conductivity, carrier concentration, carrier mobility and Seebeck coefficient of a Sb_2Te_3 film grown at $350\text{ }^\circ\text{C}$ on a $\text{Al}_2\text{O}_3(0001)$ substrate as a function of the temperature.

Table 2. Comparison of the thermoelectric and transport properties of the Sb_2Te_3 film at 300 K with other references

Growth methode	n 10^{19} cm^{-3}	σ $\text{S}\cdot\text{cm}^{-1}$	μ $\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$	S $\mu\text{V}\cdot\text{K}^{-1}$	PF $\mu\text{W}\cdot\text{cm}^{-1}\cdot\text{K}^{-2}$	Reference
Thermal evaporation	4.3	3950	558	97	33	This work
MBE	2.6	1696	402	130	29	[23]
ALD	0.24	104	270.5	146.0	22.1	[26]
Co-evaporation	1.4	775	303	160	20	[20]
Bridgman (single crystal)	8.1	4762	365	79	30	[27]

4. Conclusion

Sb_2Te_3 films were grown on $\text{Si}(100)$ and $\text{Al}_2\text{O}_3(0001)$ substrates by thermal evaporation of Sb_2Te_3 powders. Two different reactors were used and the deposition conditions (pressure, evaporator and substrate temperatures, substrate materials) were systematically varied. Sb_2Te_3 films with rough surface topology were obtained on $\text{Si}(100)$ substrates at low working pressure ($5\cdot 10^{-6}$ mbar) in a horizontal hot-wall reactor, whereas higher working pressure (20 mbar) shifted the growth zone to higher substrate temperatures and allowed the growth of highly c -oriented Sb_2Te_3 films on $\text{Si}(100)$ substrates. Epitaxial film growth was finally realized on $\text{Al}_2\text{O}_3(0001)$ substrates at higher substrate temperatures ($350\text{ }^\circ\text{C}$) and similar conditions.

The deposition process was further optimized using a cold-wall reactor with independent heaters for the substrate and the evaporator cell. The large area growth of highly stoichiometric, epitaxial Sb_2Te_3 films with low surface roughness were again grown on rather large substrate areas at a substrate temperature of 350 °C and a working pressure of 20 mbar. HRTEM investigations revealed the growth of crystalline epitaxial Sb_2Te_3 films with very low lattice defect concentrations. The *in-plane* transport properties of as-formed Sb_2Te_3 films were measured; a high carrier mobility of $558 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ and a moderate Seebeck coefficient of $97 \mu\text{V} \cdot \text{K}^{-1}$ at 300 K were observed. Based on the electrical conductivity and the Seebeck coefficient, a power factor of $33 \mu\text{W} \cdot \text{cm}^{-1} \cdot \text{K}^{-2}$ was calculated.

5. Literature

- [1] Haken W 1910 Ann. Phys. 337 291
- [2] Scherrer H and Scherrer S 1995 ed D M Rowe CRC Handbook of Thermoelectrics (New York: CRC Press) 211
- [3] Politano A, Viti L and Vitiello M S 2017 *APL Materials* 5 035504
- [4] Gooth J, Schierning G, Felser C and Nielsch K 2018 MRS Bull. 43 3 187
- [5] Moore J E 2010 Nature 464 194
- [6] Zhang J, Chang C Z, Zhang Z, Wen J, Feng X, Li K, Liu M, He K, Wang L A and Chen X Nat. Commun. 2 574
- [7] Heremans J P, Cava R J and Samarth N 2012 Nat. Rev. Mater. 2 49
- [8] Wang L L and Johnson D D 2011 Phys. Rev. B - Condens. Matter Mater. Phys. 83 1
- [9] Cao H, Venkatasubramanian R, Liu C, Pierce J, Yang H, Zahid Hasan M, Wu Y and Chen Y P 2012 *Appl. Phys. Lett.* 101 162104
- [10] Bendt G, Zastrow S, Nielsch K, Mandal P S, Sánchez-Barriga J, Rader O and Schulz S 2014 J. Mater. Chem. A 2 8215
- [11] He L, Kou X and Wang K L 2013 Phys. Status Solidi - Rapid Res. Lett. 7 50
- [12] Goncalves L M, Alpuim P, Rolo A G and Correia J H 2011 Thin Solid Films 519 4153
- [13] Goncalves L M, Alpuim P, Min G, Rowe D. M, Couto C and Correia J H 2008 Vacuum 82 12 1499
- [14] Lin J M, Chen Y C, Yang C F and Chen W 2015 Journal of Nanomaterials Article ID 135130
- [15] Lin J M, Chen Y C and Chen W 2015 2014 Journal of Nanomaterials Article ID 564954
- [16] Takashiri M, Tanaka S and Miyazaki K 2014 J. Electron. Mater. 43 1881
- [17] Völklein F, Baier V, Dillner U and Kessler E 1990 Thin Solid Films 187 253
- [18] Takashiri M, Tanaka S and Miyazaki K 2010 Thin Solid Films 519 619
- [19] Takashiri M, Tanaka S, Hagino H and Miyazaki K 2014 Int. J. Heat Mass Transf. 76 376

- [20] Zou H, Rowe D M and Williams S G K 2002 *Thin Solid Films* 408 270
- [21] Huang B, Lawrence C, Gross A, Hwang G S, Ghafour N, Lee S W, Kim H, Li C P, Uher C and Najafi C 2008 *J. Appl. Phys.* 104 113710
- [22] Bendt G, Sonntag J, Lorke A, Assenmacher W, Hagemann U and Schulz S 2015 *Semicond. Sci. Technol.* 30 85021
- [23] Peranio N, Winkler M, Bessas D, Aabdin Z, König J, Böttner H, Hermann R P and Eibl O 2012 *J. Alloy. Compd.* 521 163
- [24] Aboulfarah B, Sayah D, Mzerd A, Giani A and Boyer A 2000 *M. J. Condens. Matter* 3 76
- [25] Rieger F, Kaiser K, Bendt G, Roddatis V, Thiessen P, Schulz S and Jooss C 2018 *APL* accepted
- [26] Zastrow S, Gooth J, Boehnert T, Heiderich S, Toellner W, Heimann S, Schulz S and Nielsch K 2013 *Semicond. Sci. Technol.* 28 035010
- [27] Stordeur M, Stölzer M, Sobotta H and Riede V 1988 *Phys. Status Solidi B* 150 165

DuEPublico

Duisburg-Essen Publications online

UNIVERSITÄT
DUISBURG
ESSEN

Offen im Denken

ub | universitäts
bibliothek

This text is made available via DuEPublico, the institutional repository of the University of Duisburg-Essen. This version may eventually differ from another version distributed by a commercial publisher.

DOI: 10.1088/1361-6641/aad7a3

URN: urn:nbn:de:hbz:464-20201218-102728-4

This is the Accepted Manuscript version of an article accepted for publication in Semiconductor Science and Technology 2018, 33, 105002. IOP Publishing Ltd is not responsible for any errors or omissions in this version of the manuscript or any version derived from it. The Version of Record is available online at <https://doi.org/10.1088/1361-6641/aad7a3>



This work may be used under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 License (CC BY-NC-ND 4.0)