Electrodeposition and characterization of nano-crystalline antimony telluride thin films

J.L. Lensch-Falk a, D. Banga a, P.E. Hopkins b,c, D.B. Robinson a, V. Stavila a, P.A. Sharma b, D.L. Medlin a,*

a Sandia National Laboratories, Livermore, CA 94550, USA
b Sandia National Laboratories, Albuquerque, NM 87185, USA
b Department of Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, VA 22904, USA

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A B S T R A C T
Electrodeposition is a promising low-cost method to fabricate nanostructured thermoelectric thin films such as Sb2Te3. However, electrodeposition of crystalline Sb2Te3 without the need for additional processing and with good compositional control has presented a challenge. Here we report on the electrodeposition of crystalline Sb2Te3 thin films at room temperature from a tartaric–nitric acid electrolyte using a pulsed, potentiostatic process. The effects of synthesis conditions on the resulting microstructure and compositional homogeneity are investigated using x-ray diffraction, electron diffraction, electron microscopy, and energy dispersive x-ray spectroscopy. The composition of the Sb–Te films was found to be dependent on the interval between pulses, a result that is likely due to the slow kinetics associated with Sb2Te3 formation at the surface. We also observed a change in texture and microstructure with varied applied pulse duration: for short pulse durations a lamellar microstructure with a {0001} texture forms, whereas for longer pulse durations a more equiaxed and randomly oriented microstructure forms. The thermal conductivities of the pulsed electrodeposited films are surprisingly low at less than 2 W/K·m and are found to systematically decrease with reduced pulse time.

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1. Introduction
Thermoelectric devices, which can directly convert between heat and electricity, have numerous applications for solid-state power generation and cooling [1–3]. For applications at or near room temperature, tetradymite-structured materials based on solid solution alloys of Bi2Te3, Sb2Te3, and Bi2Se3, are currently the highest performing bulk materials [4]. Because of the potential for enhanced thermoelectric properties in nanoscale structures and interest in the development of thin film based devices for applications such as on-chip cooling [5–8] and thermal sensing [9,10], the synthesis of high quality, crystalline thermoelectric thin films based on these materials is being explored.

One approach to fabricating thin films of these materials is to employ electrodeposition. This approach is advantageous because it has relatively low cost, can be conducted at room temperature, and can be used to fill high aspect ratio geometries that are not accessible by other deposition methods [5,11,12], as is desired for the deposition of thermoelectric materials into pores to form nanowires [13]. As such, it is important to assess the ability to grow high quality and compositionally controlled crystalline films and to understand the mechanisms by which the processing conditions control the resulting microstructures and thermoelectric properties of the thin films. Sb2Te3 has been widely researched in recent years because it has been employed in several thermoelectric devices [7,14,15]. In this paper, we discuss the growth of Sb2Te3 films by electrodeposition. Synthesis of Sb2Te3 films by electrochemical means has been investigated previously by several research groups [16–22]. One common approach has been to employ continuous electrodeposition. Unfortunately, such approaches have generally led to poorly crystalline or amorphous thin films that require elevated temperature either during electrodeposition or in a post-growth annealing step to achieve crystallization. For instance, Leimkuhler et al. reported electrodeposition of this material in 2002 and observed that their room temperature deposits were amorphous; however deposition at ≈100 °C led to polycrystalline films [21]. Several studies on the electrochemistry and influence of potential and electrolyte compositions on the resulting film composition [16,20,22] and on the crystallization behavior of the as-deposited amorphous films with annealing have also been reported [17,18].

Dense, crystalline Sb2Te3 thin films have been deposited by electrochemical atomic layer epitaxy in which two different electrolytic solutions are alternatively used to deposit crystalline material [23], as much as in vapor phase atomic layer deposition. However, this method requires a more complicated laboratory setup and is more difficult to scale up than traditional electrodeposition.
A promising alternative is to employ pulsed electrodeposition. A pulsed potential (or current) during deposition has been used to achieve dense and crystalline thin films [24,25]. With this method, a single bath is utilized with a pulsed (square wave) waveform on the applied potential (or current) as shown in Fig. 1a. This pulsed potential provides a period of active deposition, \( t_1 \), and an “off” time, \( t_0 \), in which the electrochemical interface can equilibrate. During the “off” state, no current passes, and the cell is at its open-circuit voltage, \( V_{oc} \), which may drift during the course of the experiment as conditions near the electrode change. These parameters are typically expressed in terms of the “duty cycle,” which is the ratio of the “on” time (\( t_1 \)) to the total period of the pulse (duty cycle = percent of time at applied voltage = \( t_1/(t_0 + t_1) \times 100\% \)). In pulsed electrodeposition, one has control over the pulse duration for both the “on” and “off” states, the applied potential, \( V_1 \), (or applied current), and the electrolyte composition, allowing a variety of mass transport, reaction, and crystallization conditions to be achieved as compared to conventional continuous electrodeposition. Recently, C. Boulanger and co-workers have demonstrated that pulsed electrodeposition is effective for the deposition of polycrystalline thin films of \( \text{Bi}_2\text{T}_e_3 \) and \( (\text{Bi}_{1-x}\text{Sb}_x)_2\text{T}_e_3 \) [16,26,27]. Pulsed plating of these films led to decreased roughness and improved crystallinity as compared to continuously deposited films. However micrographs in that report suggest that the films were still composed of agglomerates of nanoparticles and nanofilaments, leaving room for improvement of the film density. Transport measurements indicate improvements in the Seebeck coefficient and resistivity for pulse-deposited films over as-deposited continuously electrodeposited films [26].

While pulsed electrodeposition appears promising for thermoelectric applications based on these works, key issues remain to be addressed. First, one must determine whether dense, smooth, and crystalline films of desired stoichiometry can be directly deposited without post-deposition steps. Additionally, it is important to understand how deposition conditions correlate with the resulting composition, microstructure, and texture in electrodeposited thermoelectric thin films for these materials to be used in device applications. This is particularly important for materials of the tetradymite crystal structure such as \( \text{Sb}_2\text{T}_e_3 \) and \( \text{Bi}_2\text{T}_e_3 \) since their mechanical properties [28] and thermoelectric properties [4] are highly anisotropic due to their layered crystal structure [29]. Here, we demonstrate the room temperature deposition of polycrystalline \( \text{Sb}_2\text{T}_e_3 \) thin films using pulsed electrodeposition, we examine changes in stoichiometry, microstructure, and texture associated with variations in the deposition parameters, and we correlate variations in the measured thermal conductivity of \( \text{Sb}_2\text{T}_e_3 \) films with changes in processing and microstructure.

2. Experimental details

2.1. Synthesis: electrodeposition of \( \text{Sb}_2\text{T}_e_3 \) films

\( \text{Sb–T}_e \) films were electrodeposited onto \( \text{Au/Ti/Si} \) substrates from an acidic electrolyte at room temperature with no agitation using a saturated \( \text{Ag/AgCl} \) reference electrode and a Pt sheet as the counter electrode. Each substrate, or working electrode, was prepared by evaporating 5 nm of Ti followed by 100 nm of Au on a Si wafer. Prior to electrodeposition, the prepared substrates were cleaned in an oxygen plasma (South Bay Technology, Model PC2000 plasma cleaner) for 10 min to remove any organic residue. All specimens were deposited from an electrolyte containing 16 mM antimony (III) oxide (Acrors Organics), 7 mM sodium tellurite (IV) (Alfa Aesar, 97%), 0.3 M L-(+)-tartaric acid (Fisher Chemicals), 2 M nitric acid (Fisher Chemicals), and distilled water (Barnstead Nanopure water purification system). After the deposition was complete, each sample was rinsed with deionized water to remove the residual salts and organics and then dried with nitrogen. In all \( \text{Sb–T}_e \) films described in this work, the total deposition “on” time (sum of pulses) at the applied potential was held constant at 40 s. A potentiotstat (EG&G Princeton Applied Research, Model 273A) was used for the cyclic voltammograms and electrochemical experiments.

Our selection of deposition potential was based on the results of cyclic voltammetry. Three reduction features are observed in this measurement as indicated in Fig. 1b: At \(-100 \text{mV}\), reduction of \( \text{HTeO}_2^\cdot \) to \( \text{T}_e \) occurs, at \(-300 \text{mV}\), formation of \( \text{Sb}_2\text{T}_e_3 \) occurs, and beyond \(-800 \text{mV}\) the onset of \( \text{H}_2 \) evolution is observed. Further details concerning the interpretation of these features have been published in a separate report [30]. Based on the cyclic voltammetry and the stoichiometry of electrodeposits as measured by energy dispersive x-ray spectroscopy (EDS) at potentials, \( V_1 \), between \(-250 \text{mV}\) and \(-350 \text{mV}, \(-300 \text{mV}\) was chosen as the applied potential for all experiments in this study. Potentiostatic pulsed electroplating with the rest potential at the open circuit potential and the deposition potential, \( V_1 = -300 \text{mV} \) was used to synthesize most of the films in this work. Deposition pulse durations, \( t_1 \), of 25–100 ms and rest times, \( t_0 \), of 0–4500 ms were utilized to study the effects of pulse duration and duty cycle on the composition and microstructure of these \( \text{Sb}_2\text{T}_e_3 \) films.

2.2. Characterization methods

Grazing incidence x-ray diffraction (GI-XRD, PANalytical Empyrean system, Cu K\( _\alpha \) radiation (45 kV, 40 mA, incidence angle = 0.3°–0.6°)) was utilized to determine the crystallinity and phases present in the electrodeposited \( \text{Sb–T}_e \) films. The data collection software uses the grazing incidence angle to output the collected data in terms of intensity versus 2\( \theta \), such that the GI-XRD patterns can be interpreted by the application of the standard Bragg condition. An XRD pattern was collected using the Bragg–Brentano geometry for a bulk \( \text{Sb}_2\text{T}_e_3 \) powder (Alfa Aesar, 99.999% purity) for comparison to the thin film results using the same instrument.

Preliminary compositional information was obtained using EDS in a scanning electron microscope (SEM, JEOL JSM 840). The roughness
of the film surfaces was measured using atomic force microscopy (AFM, Digital Instruments Dimension 3000) with several measurement regions on each thin film (2.5 μm x 2.5 μm measurement area at 512 x 512 pixels, acquired at a 0.5 Hz scan rate in a tapping mode). The microstructure, texture, and composition were analyzed using transmission electron microscopy (TEM, 200 kV JEOL 1010F) equipped with an EDS detector (Oxford Inc) for compositional analysis. The thickness of each film was measured by TEM with the specimen oriented such that the electron beam was parallel to the Si/Au-Sb-Te interfaces. Scanning transmission electron microscopy (STEM mode in the JEOL 1010F) with a nominally 1.6 nm diameter probe was utilized to acquire EDS spectra from individual points across the thickness of each film to confirm compositional uniformity. Quantitative analysis of the EDS spectra was carried out using Cliff–Lorimer constants determined from binary references of known composition on the same instrument [31], and using a top-hat filter to remove the background followed by a multiple least squares fit of filtered single component reference spectra [32].

Cross-sectional specimens for analysis by TEM were prepared by first adhering two film surfaces together using G1 epoxy (Gatan), and then cutting this sandwich into slices that were approximately 2.5 mm x 2.5 mm x 0.7 mm. Each slice was mechanically thinned and polished until two parallel sides and a thickness of ~100 μm were achieved. A 3 mm Au annular disk (SPI Supplies) was adhered (with G1 epoxy) to the first side of each specimen after polishing to provide mechanical support before the second side was thinned and polished. To avoid thermal artifacts on the microstructure of the films, we limited the temperature and duration of heat applied during the cure of the G1 epoxy to no more than 130 °C for 5 min. Following curing, the specimens were quenched in water. The thin sandwiches were then mechanically thinned by dimpling (Gatan 656 Dimple Grinder), and finally thinned to electron transparency by Ar⁺ ion milling (Fischione 1010) at temperatures below ~133 °C. We have previously found that rigorous control of the temperature and duration of the ion milling step is critical to avoiding ion milling artifacts in TEM specimens prepared from telluride-based thermoelectric materials [33,34].

Our measurements of film properties focused on the cross-plane thermal conductivity; we did not attempt to measure the electronic transport properties on these particular films due to the presence of the electrically conductive underlying Au coating on the substrate which would introduce artifacts. The thermal conductivities of the Sb₂Te₃ films were measured with time domain thermoreflectance (TDTR) [35] at room temperature (296 K). TDTR and appropriate analyses accounting for pulse accumulation when using a Ti:sapphire oscillator have been detailed by several groups previously [36–40]. Our specific experimental setup is described in detail elsewhere [39]. In short, TDTR is a pump–probe technique in which laser pulses emanate from a Spectra Physics Mai Tai laser with 90 fs pulses at an 80 MHz repetition rate. We delayed the time in which the probe pulse reaches the sample with respect to the pump pulse with a mechanical delay stage that gives ~4 ns of probe delay. The pump path was modulated at 11 MHz and the ratio of the in-phase to out-of-phase signal of the probe beam from a lock-in amplifier (-V programmed at -V out) was monitored. Our pump and probe spots are focused to 15 μm radii at the sample surface; at these sizes when modulating at 11 MHz, we should be negligibly sensitive to any in-plane transport in Sb₂Te₃ films [39,41], decreasing the uncertainty associated with determining the cross-plane thermal conductivity. Typical uncertainties due to the different locations on the samples or from sample to sample were less than 12% (calculated from the standard deviation among all the TDTR scans on a given sample type). We fit the TDTR data with a model that accounts for pulse accumulation in a layered system. Due to the relative thicknesses of the Sb₂Te₃ films and their low thermal conductivities, we are primarily sensitive to the thermal conductivity of the films at this modulation frequency [39], reducing uncertainty due to thermal boundary conductances.

3. Results

Pulsed electrodeposition was found to improve the composition, homogeneity, and crystallinity in the Sb-Te electrodeposits as compared to continuous electrodeposition. All of the pulsed deposited films appeared metallic and shiny, providing the first indication that these films are likely uniform and dense. AFM measurements confirmed that the pulse deposited films are dense and smooth with a root mean square surface roughness of less than 6 nm. Furthermore, XRD and TEM measurements showed that when pulse deposited (t₁ = 100 ms, t₀ = 4.5 s) was utilized, a polycrystalline thin film resulted (Fig. 2a,c). In the GI-XRD pattern shown for the pulse deposited film in Fig. 2a, many peaks are present, all of which correspond to those expected for the Sb₂Te₃ tetradymite crystal structure [29] and observed for the bulk Sb₂Te₃ powder. The TEM micrograph (Figs. 2c and 6a) and associated electron diffraction pattern (Fig. 6c) confirm that the material is polycrystalline Sb₂Te₃. STEM-EDS indicated that the composition within the pulse deposited film is stoichiometric and uniform throughout the film thickness (Fig. 3b), as will be discussed in Section 4.1.

In contrast, by optical inspection, the specimen deposited by continuous electrodeposition from the same bath chemistry appeared cloudy and gray (more diffusely reflected light), which was a first indication that the quality of this film was poor in comparison to the pulsed electrodeposited films. X-ray diffraction of the thin film deposited with a continuously applied voltage suggested that a mixture of amorphous and crystalline material is present as indicated by a large, broad background and a single peak consistent with the highest intensity Sb₂Te₃ peak. (0115) (Fig. 2a). Cross-sectional TEM (Fig. 2b) confirms that this film is composed of small crystallites (possibly Sb₂Te₃) in an amorphous matrix. This film was found to be Sb-rich and non-stoichiometric (overall average film composition ≈84 at.% Sb) and uniform throughout the film thickness (Fig. 3b).
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Further investigation of the composition across the thickness of the film was studied by collecting STEM–EDS line scans (Fig. 3b). While the sample deposited at the 2% duty cycle was found to have a uniform and stoichiometric composition across its thickness, this was not the case for films deposited at higher duty cycles. These measurements showed that the composition near the Au/Sb–Te interface is stoichiometric for the first 10 nm before gradually decreasing (over approximately 30–50 nm) to a constant composition for the remainder of the film thickness at the Te deficient values in the films deposited at the 10% and 50% duty cycles. This large decrease in Te composition with increased duty cycle occurs in conjunction with large decreases in the film thickness (Fig. 3a), indicating that the differences in thickness are likely associated with the deposition of decreased amounts of Te while the amount of Sb deposited in each of these films is nearly constant.

3.2. Effects of varying pulse durations on electrodeposited Sb2Te3 films

In the second set of experiments, we varied the applied pulse duration while keeping the duty cycle constant at 2% to determine whether the applied pulse length affects the stoichiometry and microstructure of the resulting films. Holding the duty cycle constant at 2% while decreasing the duration per pulse at the applied voltage, t₀, from 100 ms to 25 ms resulted in films with compositions consistent with Sb2Te3 as determined by EDS in both the SEM (Fig. 4) and TEM. Furthermore, STEM/EDS measurements indicate that the composition is uniform throughout the thickness of the electrodeposited films (Fig. 3b). GI-XRD confirmed that the films are polycrystalline Sb2Te3 with the tetradymite crystal structure as each of the peak positions correspond well to the expected values (Fig. 5b).

Through a more detailed analysis of the XRD results we also assessed the texture of these thin films, focusing primarily on the films with pulse times of 100 ms and 50 ms. Sb2Te3 (R3m, a = b = 4.264 Å, c = 30.458 Å, α = β = 90°, γ = 120°) [29] has a layered crystal structure with rhombohedral symmetry as illustrated in Fig. 5a. The XRD results in Fig. 5b–d, show a marked change in the relative peak intensities with a reduction of t₀ from 100 ms to 50 ms. For the 100 ms film, the pattern is well matched to the expected peak intensities for a random polycrystalline Sb2Te3 sample, but for the films deposited with t₀ = 50 ms, the intensity of the (0001) peaks is increased while the intensity of the (0115) peak is decreased. A similar increase in the (0001) peak intensities is observed for the sample deposited with t₀ = 25 ms.

Since we employed a grazing incidence geometry, it is important to consider the orientation of the sampled planes with respect to the film surface when discussing texture, as for each 2θ value, only planes at a particular angle from the surface will satisfy the Bragg condition. Variations from the expected powder pattern at low 2θ values can be reasonably approximated as indicating a textural preference for a certain plane since these planes are nearly parallel to the film surface (within ± 20 = 30° and an incidence angle of 1°). With these considerations, the GI-XRD results indicate that the films deposited with t₀ ≤ 50 ms (at 2% duty cycle) have a slightly preferred orientation along the (0001) planes nearly parallel to the substrate surface.

An additional feature is observed in the XRD patterns shown in Fig. 5b,d. Here, splitting of the (0115) peak is observed, with the

Fig. 4. Composition is shown to be constant and stoichiometric for Sb2Te3 at t₀ = 25–100 ms and a constant duty cycle of 2% as determined by SEM–EDS measurements.
intensity of the higher angle peak increasing with decreasing $t_1$. Similar peak splitting has been reported due to the presence of both $\text{Sb}_2\text{Te}_3$ and a metal rich $\text{Sb}_3\text{Te}_4$ phase with a structure similar to that of $\text{Sb}_2\text{Te}_3$, except that it has 7-layer packets instead of 5-layer packets [42] (the 5-layer $\text{Sb}_2\text{Te}_3$ structure is shown in Fig. 5a). Thus, this effect could similarly indicate co-existence of a slightly metal rich phase. Although we do not observe such clear peak splitting in the other features of the XRD pattern, we note that because the peaks in the pattern and the similarity in the crystal structures, the other features of the XRD pattern, we note that because the peaks in the pattern and the similarity in the crystal structures, a comparison of the microstructure resulting from a 100 ms pulse duration with that of a 50 ms or 25 ms pulse duration shows a transition to long and thin lamellar features with a reduced pulse duration (Fig. 6d,e,g,h). In many cases, particularly near the substrate, the lamellar features are aligned nearly parallel (within 20°) to the substrate surface. These lamellar grains have been observed with sizes up to 750 nm wide and 40 nm thick. From the deposition rate, we know that less than 1 nm is deposited per pulse; thus each grain is deposited over a few to tens of pulses. Qualitatively, the size of the lamellar features in the thin film deposited with a 25 ms pulse duration is smaller or similar in size to those present in the film deposited with a 50 ms pulse duration.

Higher magnification TEM micrographs from the $t_1 = 50$ ms and 25 ms samples and associated electron diffraction patterns (Fig. 6e,f,h,i) show that these lamellar features are aligned with their large flat edges nearly parallel to the (0001) planes (short dimension parallel to the [0001] direction). The electron diffraction patterns indicate that the (000r/) planes are aligned within a very narrow range of angles for all three samples suggesting some degree of texturing with the (0001) planes nearly parallel to the substrate surface for all three pulse durations (25, 50, and 100 ms). Consideration of the other reflections in the electron diffraction patterns, particularly the angular spread of the reflections from the {0115}, {1010}, and {1120} families of planes, suggests a higher degree of in-plane texturing in the thin films deposited with a 25 ms pulse duration is smaller or similar in size.

3.3. Thermal conductivity measurements on electrodeposited $\text{Sb}_2\text{Te}_3$ films

Finally, we investigated the thermal conductivities of these films. We focused specifically on the series of films grown with decreased applied pulse duration at a constant duty cycle of 2%. As shown in Fig. 7, the measured thermal conductivities for these $\text{Sb}_2\text{Te}_3$ films are lower than 2 W/K·m which is close to or below the value along the c-axis in single crystalline $\text{Sb}_2\text{Te}_3$ [4]. As we discussed in Section 4.2, this low thermal conductivity can be rationalized in terms of the observed microstructural variations.

4. Discussion

The results presented above demonstrate the sensitive dependence of composition, microstructure, and thermal transport properties of the deposited Sb–Te films on the electrodeposition conditions. In this section, we suggest possible mechanistic and thermodynamic reasons for these observations and discuss the correlation of this microstructural evolution with systematic changes in the thermal transport behavior.

4.1. Mechanistic and thermodynamic reasons for the observed compositional and microstructural variations

Consider first the dependence of composition on the pulse duration and duty cycle. In general, during each electrodeposition pulse, several inter-related processes are expected to occur. These processes include mass transfer, chemical reactions (including reduction of electrolyte species at the electrode interface), and adsorption and desorption of species on the substrate surface. Following each applied
pulse is an “off” time in which the electrolyte solution recovers as adsorption, desorption, and migration processes continue to occur.

The initial decrease in Te content observed in the EDS linescans in Fig. 3b leads us to believe that its deposition is mass transport-limited, and that its concentration becomes depleted near the interface when short “off” times (or high duty cycles) are used. This interpretation is supported by the observation that deposition occurs at potentials more negative than the Te-associated peak in Fig. 1b. Because $V_1$ is near the top of the Sb peak in Fig. 1b, one can expect that the deposition of Sb is more limited by chemical kinetics at the surface than Te, and less concentration depletion of Sb occurs near the surface. Calculations estimating the deposited mass of Sb and Te deposited in each film confirm that similar masses of Sb have been deposited in each film (based on the measured film thickness and composition, and using the atomic densities of Sb$_2$Te$_3$ and Sb). This observation of decreased Te incorporation during electrodeposition with short “off”, or recovery, times is likely indicative of the long times needed (>450 ms) to ensure sufficient mass transfer of Te, which is in the diffusion-limited regime at the deposition potential, $V_1$ [43–45]. This depletion of the electrolyte with short “off” times (high duty cycles), is schematically depicted in Fig. 8a. Our results suggest that the existence of this “off” time, which differentiates continuous plating from pulsed plating, leads to more uniformity in film composition and crystallinity throughout the electrodeposited thickness as the electrolyte is given time to recover its equilibrium concentrations.

Our observations also found significant changes in the microstructure and texture with the pulsing conditions utilized during electrodeposition. First, we observed a decrease in grain size with decreased pulse duration. This can be expected if the number of nucleation events per pulse were roughly constant (as if they were more likely at the beginning of a pulse, when near-surface concentrations...
are highest) but shorter pulse times allow less time for grain growth. Second, we observed a change in grain shape, from somewhat equiaxed grains to lamellar features, as the applied pulse duration was decreased. This change in grain shape was also associated with a variation in texture, with the film adopting a stronger (0001) texture. With shortened applied pulses, one expects that fewer atoms are deposited per pulse such that the likelihood of burying adatoms in unstable bonding configurations is reduced. Additionally, the subsequent “off” time allows atoms in unstable bonding configurations to desorb from the film surface or to migrate along the substrate surface to more stable positions as depicted in Fig. 8b. These processes may lead to a more thermodynamically favorable orientation in the resulting thin film, raising the question of what morphologies and microstructures are stable in the Sb₂Te₃ tetradymite structure.

As seen in Fig. 5a, the Sb₂Te₃ crystal is made up of three quin- tets composed of –Te(1)–Sb–Te(2)–Sb–Te(1)– layers along the c-direction. Within each 5-layer quintet, the atoms are covalently bond- ed, while the Te(1)–Te(1) layers between quintets are bound through weaker Van der Waals interactions [46]. This weak interaction allows such tetradymite type structures to easily cleave along the (0001) planes between the Te(1)–Te(1) layers and form low energy (0001) facets. Indeed, a number of reports have shown crystal shapes in these materials with large (0001) facets [47–50]. In particular, both Liu et al. [47] and Liao [48] have observed the formation of nanoscale plates with large (0001) facets during electrocrystallization of Bi₂Te₃. Fan et al. demonstrated the synthesis of [0001] oriented plate-like Bi₂Te₃ nanoparticles by a microwave assisted wet chemical method [49]. Additionally, chemical vapor transport has been used to convert...
films of Bi nanoparticles into Bi2Te3 films composed of (0001) nanoparticles [50]. Since the formation of large (0001) facets is an energetically favorable configuration in the tetradymite crystal structure, the formation of such a lamellar microstructure might be expected to occur under conditions that favor a more energetically stable microstructure and texture, such as reduced pulse duration (t1).

4.2. Correlation of thermal conductivity with microstructure

Given the changes in microstructure and texture observed in these Sb2Te3 thin films, one might expect the thermoelectric properties to vary as well. We focus here on the thermal conductivity. We note first that the measured thermal conductivities for all three Sb2Te3 films are low in comparison with bulk Sb2Te3. In a randomly oriented polycrystalline thin film, the thermal conductivity is expected to follow
\[ \kappa_{\text{poly}} = \frac{\kappa_c}{3} + 2\kappa_{ab}/3, \]
where \( \kappa_{\text{poly}} \) is the thermal conductivity of the sample, \( \kappa_c \) is the thermal conductivity along the c-axis of a single crystal, and \( \kappa_{ab} \) is the thermal conductivity in the ab plane. This estimate assumes no grain boundaries along the out-of-plane direction, and corresponds to the gray shaded area in Fig. 7 (this region is wide since \( \kappa \) in Sb2Te3 depends on the carrier concentration) [4,51,52]. A textured polycrystalline Sb2Te3 film would be expected to have a thermal conductivity that falls between \( \kappa_c \) and \( \kappa_{ab} \). The measured values for the films deposited with \( t_1 = 100 \) and 50 ms are above the value expected along the c-axis in Sb2Te3. These low values are consistent with films that are mostly textured with the c-axis perpendicular to the film surface as observed for \( t_1 = 100 \) ms. Surprisingly, the lowest measured thermal conductivity (for \( t_1 = 25 \) ms, \( \Delta t = 0.433 \) W/K m) is below that of the minimum reported c-axis value for single crystal Sb2Te3 and approaches the theoretical expectation of pores in the Sb2Te3 [61].

Correlation of thermal conductivity with microstructure

The thermal conductivity of these thin films was found to be extremely low (less than 2 W/K·m) and to systematically vary with the electrodeposition conditions and microstructure. The best thermoelectric materials have similarly low thermal conductivities, which would suggest that further work to explore the dependence of the electrical properties with deposition conditions and microstructure would be fruitful.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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