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APPLIED PHYSICS BACHELOR PROJECT

Conductivity of PLD Grown Telluride Films

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Abstract

In this work, electrical conductivity of pulsed laser deposition (PLD) grown telluride films are investigated, namely Sb_2Te_3 and GeTe. The two films are known for their thermoelectric properties which can be quantified by looking at thermoelectric figure of merit which is linear to the electrical conductivity. It has been observed that the electrical conductivity Sb_2Te_3 single layer decreases with increasing temperature, showing a metallic-like conducting behaviour in which resistivity is proportional to temperature. Conversely, GeTe single layer shows more semiconducting behaviour, that their electrical conductivity increases with temperature. It also has been observed that conductivity of crystalline GeTe shows a sharp jump, which is similar to the feature of amorphous to crystalline. When these two layers, Sb_2Te_3 and GeTe, are stacked on top of each other, creating superlattice-like films, the conductivity is dominated by GeTe. The electrical conductivity of this superlattice-like film, with four times more GeTe single layers than the Sb_2Te_3 single layers, was found to be 600 S/cm at room temperature, giving a low resistivity upon intermixing between the constituent layers of superlattice-like film. By doing some optimization of the superlattice-like films constituent layers thickness under some conditions, a high figure of merit of this system can be achieved.

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1 Introduction

Thermoelectric materials have been used in many applications such as solar cells (1), thermocouples (2), and cooling components (3). This kind of materials are capable of harvesting energy from heat or waste heat. The phenomena are also known as Seebeck effect, where voltage builds up due to applied temperature, and Peltier effect, when there is a temperature difference induced by applied current. One way to quantify the efficiency of thermoelectric materials is to consider their figure of merit. This is given by $zT = S^2 \cdot \sigma \cdot T / \kappa$ where z is the dimensionless figure of merit, T is temperature, S is the Seebeck coefficient, σ is electrical conductivity and κ is the thermal conductivity.

It has been demonstrated (4) that bismuth-antimony-telluride ($\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$) superlattice thin films could achieve high efficiency by controlling the thin films electron and phonon transport. On top of that, $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ heterostructures are also versatile in which their charge carriers can be tuned in precise manner (5). Another material that strongly shows thermoelectric behaviour is germanium telluride (GeTe). One of the compelling features of this material is its atomic structure that also changes in different temperature which is called phase change properties. This occurs when the phase of materials switches from amorphous to crystalline structure (6), (7). In memory elements information is written and destroyed during the transition of the two phases. GeTe , which are commonly p-type semiconductor, have also been observed to be superconducting (8), which is then a great interest for thermoelectric applications.

There are several ways to increase thermoelectric figure of merit, one can decrease thermal conductivity by phonon and band engineering (9), (10) or increase electrical the overall performance by exploring other thermoelectric materials. This is then what drives the search for superlattice-like structure with GeTe in order to obtain a high thermoelectric figure of merit. With the superlattice-like structure, there is an addition of degree of freedom in the study of thermoelectric properties. In this work, the electrical conductivity of $\text{GeTe}/\text{Sb}_2\text{Te}_3$ superlattice-like films dependency on their constituent layers thickness is investigated by measuring the sheet resistance of telluride thin films using van der Pauw method.

2 Background Information

2.1 Thermoelectric Materials

The phenomenon was first observed by Seebeck (11) where he found that a change in temperature between two junctions results in a potential difference between two points. The two junctions are connected by two different metals where one end is heated up.

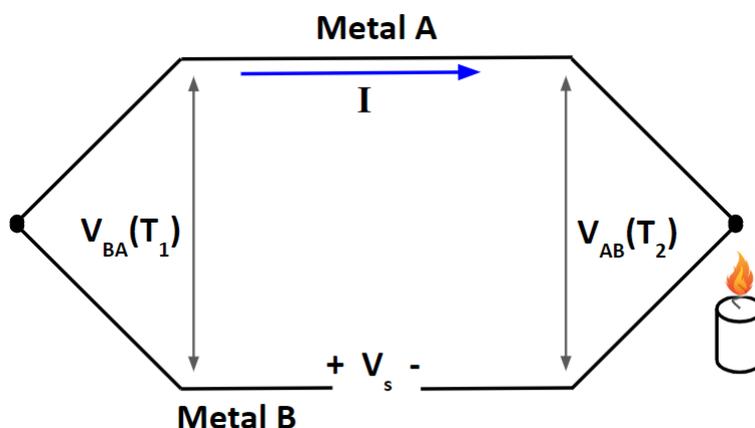


Figure 1: Experimental setup when thermoelectric behaviour first observed by Seebeck

The difference in temperature between two junctions results in diffusivity of charge carriers, creating a constant current running from one junction to another which leads to potential built up between the two metals, denoted by V_{BA} and V_{AB} in Figure 1. This is proportional to Seebeck voltage through Seebeck coefficient. The relation is found to be

$$V_s = -S\Delta T \quad (1)$$

Where V_s and S are Seebeck voltage and coefficient, respectively.

By using the same setup as when Seebeck observed thermoelectric properties, electrical conductivity of thermoelectric materials can be obtained. In this setup, two probes are needed to measure the voltage, V in unit of volts, when current, I in unit of amps, is run through at different temperatures. From Ohm's law, the resistance of materials will be just be $R = V/I$ in unit of Ω . Once the resistance is obtained, resistivity (12) is obtained by also considering the three dimensional geometry given by

$$\rho = \frac{R \cdot w \cdot d}{l} \quad (2)$$

Where ρ is the resistivity in units of Ωm and w, d, l are width, thickness, length of the material given in unit m . The electrical conductivity, σ in units of S/m , is then

$$\sigma = \frac{1}{\rho} \quad (3)$$

2.2 Electrical Properties of GeTe and Sb₂Te₃

Under different conditions, electrical conductivity is also different for the same materials which is summarized in Table 1. For all values of electrical conductivity, the obtained electrical conductivity is under different temperature conditions, otherwise stated.

Material	Deposition	Thickness (nm)	Electrical conductivity (S/cm)	Ref
Sb ₂ Te ₃	Molecular beam epitaxy	1150	162	(13)
Sb ₂ Te ₃	Electrodeposition	2200	1064	(14)
Sb ₂ Te ₃	Coevaporation	700	200	(15)
Sb ₂ Te ₃ *	Ion beam sputtering	(not given)	1060	(16)
Sb ₂ Te ₃ *	Atomic layer deposition	128	104	(17)
GeTe	Evaporation and sputtering	589 (bulk)	4080	(18)
GeTe	Atomic layer deposition	35	1000	(19)
GeTe	Magnetron sputtering	80	1250	(20)
GeTe*	Pulsed laser deposition	60	1600	(21)

Table 1: Electrical conductivity of Sb₂Te₃ and GeTe under room temperature. * denotes the electrical conductivity that has been measured not in room temperature.

As can be seen from the figure above, under different deposition technique and thickness, each Sb₂Te₃ and GeTe films have different electrical conductivity, in which even the relation between the thickness of the films and the electrical conductivity cannot be obtained through literature review.

3 Samples and Method

3.1 Thin Films

There are five different samples measured and each sample is made of different compositions. The thin films are grown using pulsed laser deposition technique on top of SiO layer with a thickness of 300 nm, width and length of 1 cm. The deposition technique was used to deterministically control the thickness of atomic layers within thin film.

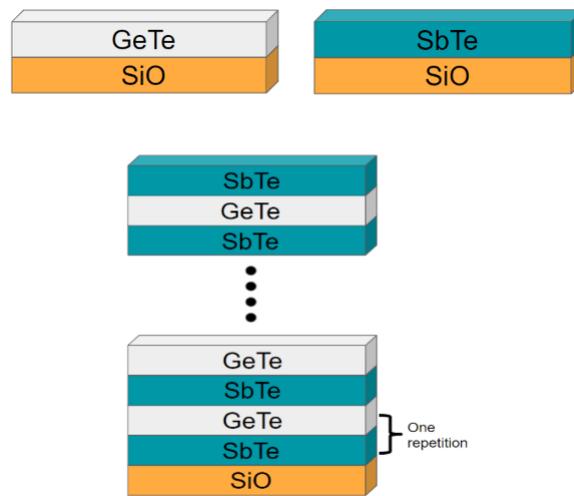


Figure 2: Single layer of GeTe (top left), single layer Sb_2Te_3 (top right) and superlattice-like film composition.

There are two single lattice thin film samples and three superlattice thin film samples. The single lattice samples are GeTe and Sb_2Te_3 with thickness of 77.8 nm and 110 nm, respectively, using 10000 pulses deposition. For the superlattice-like samples, GeTe layer is deposited on top of Sb_2Te_3 , resulting to one repetition. Each superlattice-like sample consists of six repetitions and another layer of Sb_2Te_3 is deposited on top of the six repetitions that serves as a cap of the superlattice. The capping then protects the superlattice as GeTe is easily evaporated and oxidized. Three different thicknesses of superlattice are measured, 34.8 nm, 45.4 nm, and 60.1 nm with GeTe deposition pulses of 300, 600, and 1200 pulses, respectively, while Sb_2Te_3 deposition pulses are kept constant at 300 pulses.

3.2 Van der Pauw Method

In 1958, van der Pauw (14) invented a method to measure specific resistivity of a material. He showed that his method holds for a flat sample of arbitrary shape that he proved using conformal mapping of two dimensional fields.

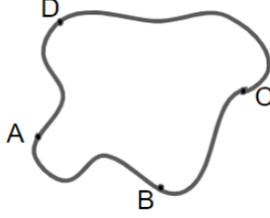


Figure 3: Four points measurement of flat and arbitrary shape.

He showed that the relation between the specific resistivity and the four points of measurement is invariant under mapping. This relation is given by

$$\exp\left(-\frac{\pi \cdot R_v \cdot d}{\rho}\right) + \exp\left(-\frac{\pi \cdot R_h \cdot d}{\rho}\right) = \exp\left(-\frac{\pi \cdot R_v}{R_s}\right) + \exp\left(-\frac{\pi \cdot R_h}{R_s}\right) = 1 \quad (4)$$

Where R_h is the horizontal resistance, R_v is the vertical resistance and resistivity divided by thickness, ρ/d , gives the sheet resistance, R_s , in units of $\Omega/area$. This equation cannot be solved analytically and because of that, R_s can only be obtained by solving the equation numerically.

In order to use van der Pauw method, there are several conditions need to be fulfilled. Firstly, the electrical contacts are at the circumference of the material and they are equally spaced. These four contacts have to be sufficiently small. The thickness of the sample has to be homogeneous and the surface is singly connected (does not have isolated holes). Statistically, this technique would give less error from the electrical contact, compared to Seebeck measurement in which only two probes are used. The two-point probe measurements would have more error from contact resistance as in the case of four-point probe measurements, the error from each contact resistance is compensated by averaging the error throughout the measurement. This method can also be used to determined Hall coefficient and charge carriers density that are out of the scope of this experiment but extremely useful to further investigate transport properties of a material.

3.3 Experimental Setup

The setup consists of stage, probes, and data acquisition devices. Samples are placed on the stage where a heat contact is present in between using silver glue, otherwise stated. The four probes are the measuring agent in which they are clamped to vacuumed microcontrollers that control precisely the movement of the probes in three directions. The probes are then connected to the multimeters that are controlled by the computer.



Figure 4: Electrical contacts (with and without electrodes) denoted by A, B, C, D using probes. One of the two horizontal resistance is obtained by dividing voltage drop between points C and D by current run through points A and B. One of the vertical resistance then comes from the voltage drop between points A and C and current from B and D.

The measurement was conducted by flowing current on two of the probes, at one side of the sample, vertically and/or horizontally but not diagonally. This means that there are eight combinations of current flow. For each combination, the current are run through that are positive (+1 mA), zero or no current, and negative (-1 mA). While current flows, the other two probes on the other side measure the voltage difference. The resistance is then achieved using Ohm's law.

Electric contacts are required in the measurement to make sure that the current actually flows and they are positioned in circumference as illustrated in Figure 4. Electrical contacts can be done in two ways, with and without electrodes. Without electrodes, the probes are touching the sample directly and with electrodes, the probes are touching the sample via electrodes composed of gold (Au) and titanium (Ti) deposited using masking technique.

There are several ways to check whether a contact is made or not. Firstly, the reflected image of the probe on the sample can be seen and when there is not any gap between the probe and the reflected image, the probe in a sense is touching or

making a contact to the sample. Also, there would be enough resistance experienced on the microcontroller while lowering the probe, if a contact was made. Lastly, one of the combinations of the current flow can be run to see the resistance of the contact, if the resistance is extremely large, it means that there might be some probes out of four probes that do not touch the sample.

4 Result and Discussion

Sheet resistance, R_s , of single layers as well as superlattice-like films have been measured using van der Pauw method in room temperature range to typically 210°C. From these results (given in Appendix), electrical conductivity is obtained. This is done by multiplying the sheet resistance with the appropriate geometry of the sample to find resistivity, ρ , first. Since the width to length ratio, w/l , of all samples that have been measured in this project is 1, ρ is then $R_s \cdot d$. Electrical conductivity, σ , is then the reciprocal values of ρ .

4.1 Single Layers of GeTe and Sb₂Te₃

Single layer of Sb₂Te₃ and GeTe has been measured, without electrodes, individually in order to obtain their electrical conductivity values. Upon first heating cycle using four-point probe measurement, Sb₂Te₃ electrical conductivity decreases as temperature increases as shown in Figure 5a. This shows a general metallic behaviour where resistivity increases with temperature. In theory, the relation between resistivity and temperature should be linear, which is not observed here. There seems to be some non-linearity measured which might show that Sb₂Te₃ is not completely metallic. In the second and third heating cycle electrical conductivity is lower than the first heating cycle that there is an offset after the first measurement.

Compared with the results with two-point probe measurements, shown in Figure 5b, it is confirmed that Sb₂Te₃ electrical conductivity decreases as the single layer is heated up. There are also some offset after first cycle heating observed in this method. However, Sb₂Te₃ single layer electrical conductivity shows metallic behaviour as the resistivity is highly linear with temperature measured in two-point probe method. The different conducting behaviour between the two methods could be due Sb₂Te₃ narrow band gap (22) in their thin films forms which might cause different charge carrier diffusion between the two methods that results in different conducting behaviour. Referring to literature (23), the results from four-point probe

measurement give closer values of electrical conductivity under room temperature and high temperature.

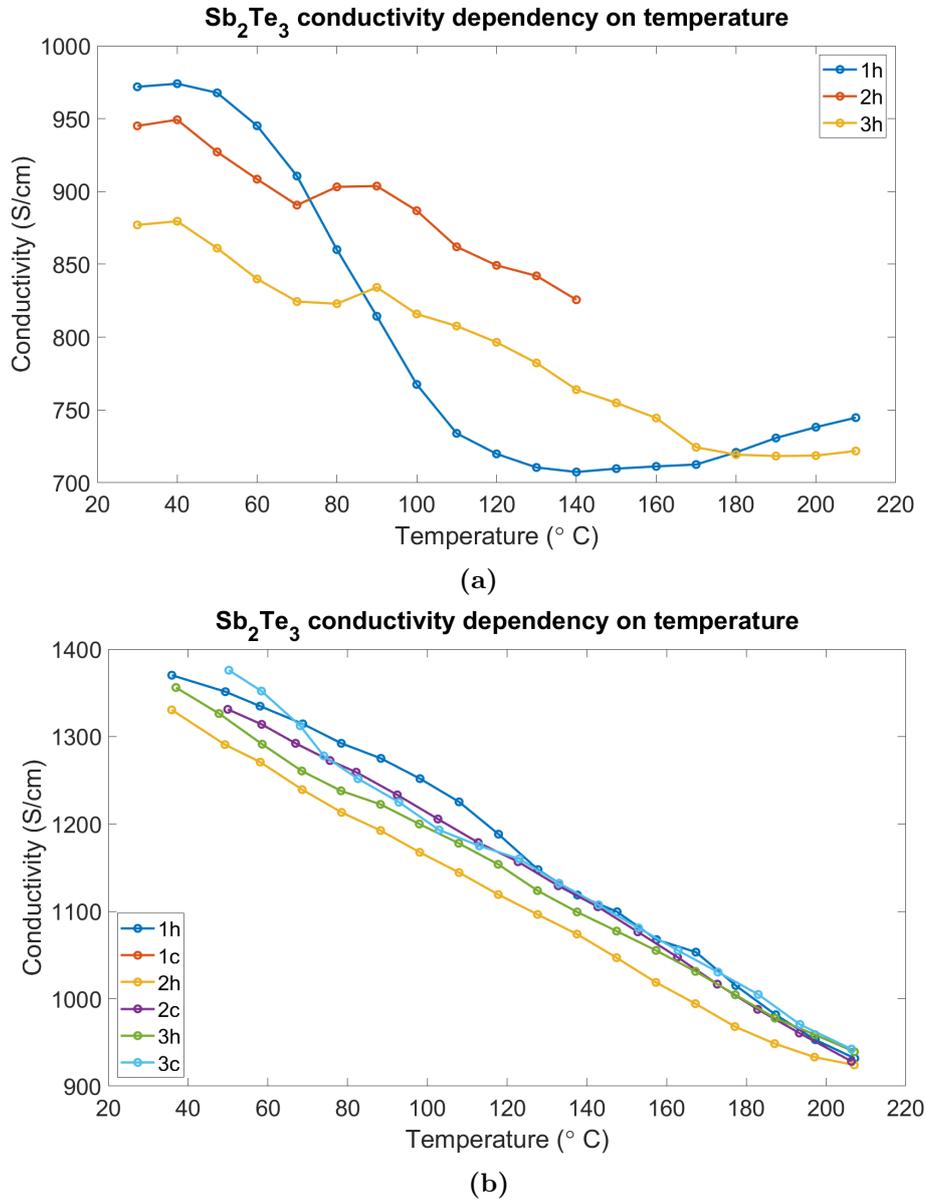
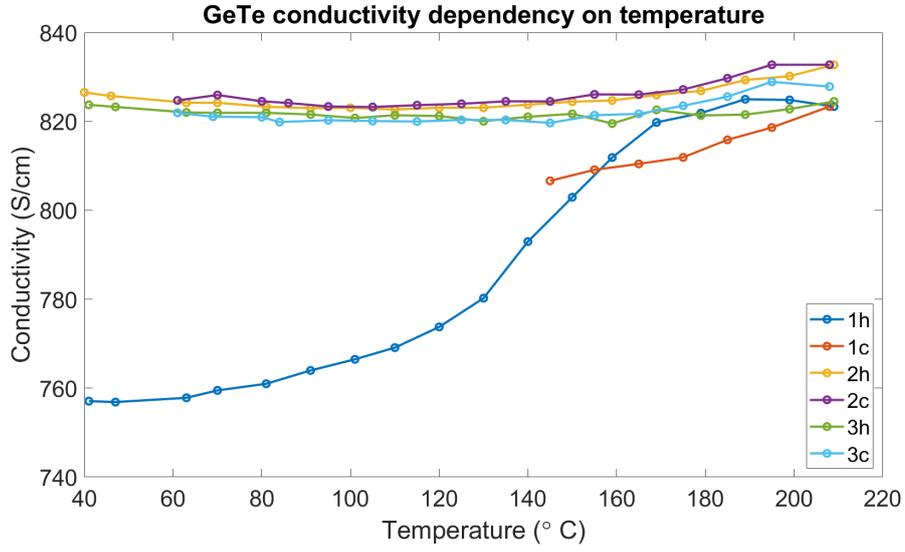
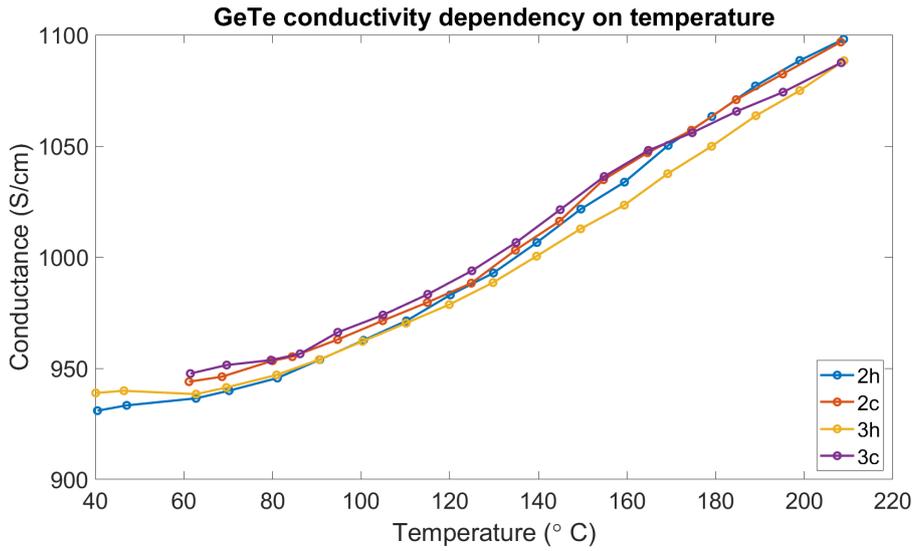


Figure 5: Dependency on temperature of Sb_2Te_3 electrical conductivity measured in three cycles using four-point (a) and two-point probe method (b).

In contrast to Sb_2Te_3 , electrical conductivity of GeTe increases with increasing temperature. This can be seen clearly in the first cycle heating of four-point probe measurement, shown in Figure 6a, that GeTe electrical conductivity shows semiconducting properties, where conduction is governed by holes (23).



(a)



(b)

Figure 6: Dependency on temperature of GeTe electrical conductivity measured in three cycles using four-point (a) and two-point probe method (b).

After first cycle heating, GeTe electrical conductivity stabilizes. This resembles the phase change properties in GeTe, as observed in other works ((21), (20)), although it occurs more commonly in amorphous GeTe, where in this case GeTe is crystalline. However, it has been proven by x-rays powder diffraction (XRD) measurements that the increase of electrical conductivity comes from tellurium evaporation as there were more tellurium than germanium in GeTe single layer

during deposition. Similarly, GeTe electrical conductivity increases with increasing temperature using two-point probe measurements, shown in Figure 6b. In this case, GeTe electrical conductivity from two probes measurement gives closer values to the literature (19).

For both Sb_2Te_3 and GeTe, four-point probe measurement leads to smaller values of electrical conductivity. The decrease in electrical conductivity in four-point probe measurement could be due to more contact resistance in the measurement that comes from the addition of probes, compared with two-point probe measurements. Also, during cooling cycles, four points measurement does not seem to improve the accuracy of the results. This might be due to the heating contact which might not be a good cooling contact for the system.

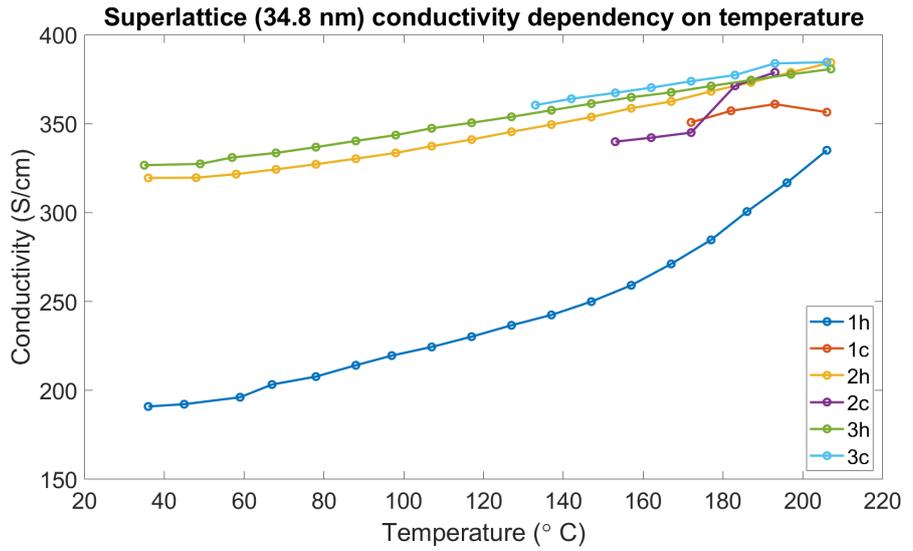
When the results of single layers are compared to the electrical conductivity values in previous section, the difference is indeed huge although they are in the same magnitude. This difference might be due to several reasons, but one of the most acceptable reasons is the fact that there are several cycles measured within one sample that might influence the fundamental structure of the material. On top of that, it is clear that even for the same deposition techniques, there might be different parameters used which then changes the stoichiometry, grain size, and/or morphology of the film significantly.

4.2 GeTe/ Sb_2Te_3 Superlattice-like Films

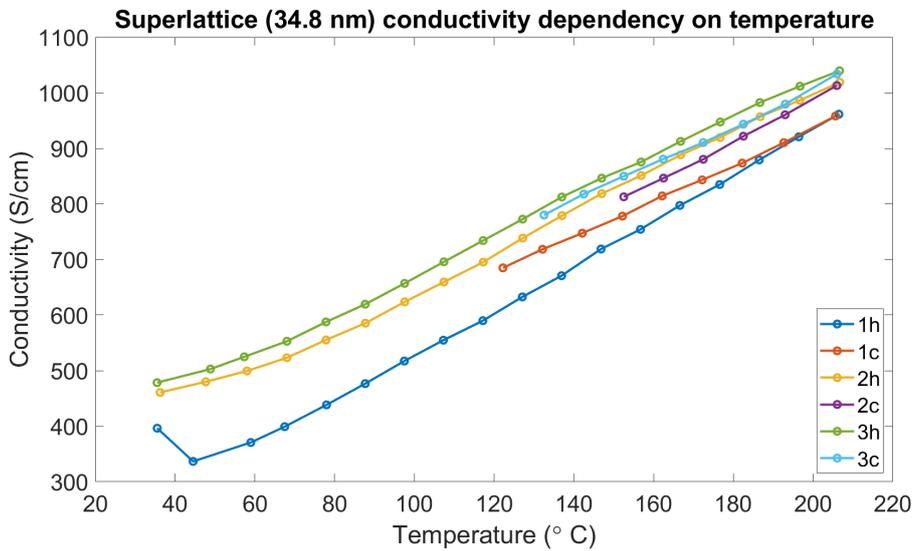
The electrical conductivity of superlattice-like films generally increases with increasing temperature for different thicknesses measured in four-point probe measurement. Similar behaviour of GeTe/ Sb_2Te_3 electrical conductivity is also observed when measured in two-point probe measurement. This already shows that GeTe is dominating the behaviour of electrical conductivity in the GeTe/ Sb_2Te_3 superlattice-like films.

For the thinnest superlattice-like films with pulse number ratio between GeTe and Sb_2Te_3 of 1, two different samples in which each of the sample is measured using different methods, namely van der Pauw method (Figure 7a) and Seebeck method (Figure 7b), without any electrodes deposited on to the sample. The difference of electrical conductivity at room and high temperature, $\Delta\sigma$, is found to be around 150 S/cm in the first heating cycle, as shown in Figure 7a for four-point probe measurement. In the next cooling cycle, the electrical conductivity jumps to a higher value than in the first heating cycle although measured in the same

temperature of 210°C, denoted by 1c in Figure 7a. Only in the second and third cooling cycle, electrical conductivity stabilizes at a higher value than the first cycle heating. The same cooling problem is also observed in both methods for the thinnest GeTe/Sb₂Te₃ superlattice-like films, that electrical conductivity cannot simply obtained during cooling cycles.



(a)



(b)

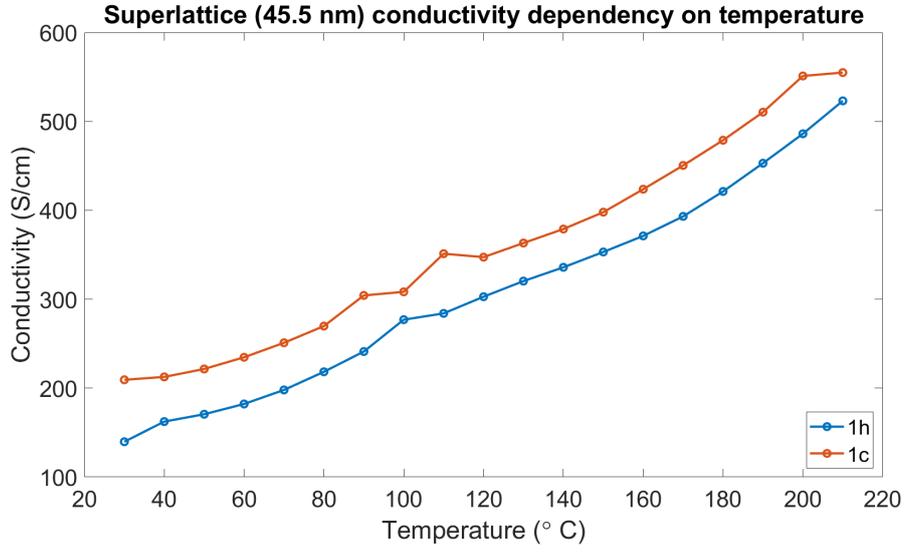
Figure 7: Dependency on temperature of the thinnest superlattice-like films electrical conductivity measured in three cycles using four-point (a) and two-point probe method (b).

The electrical conductivity of GeTe/Sb₂Te₃ superlattice-like films when measured in two-point probes measurement, shown in Figure (Figure 7b), is higher than the results from four-point probe measurement, resulting in a higher $\Delta\sigma$ value of around 600 S/cm. In this case, electrical conductivity, which are observed in all three cycles, as a function of temperature shows a linear relation. Also, another similarity of the results between the two methods that there is an offset in the measured electrical conductivity after first heating cycle.

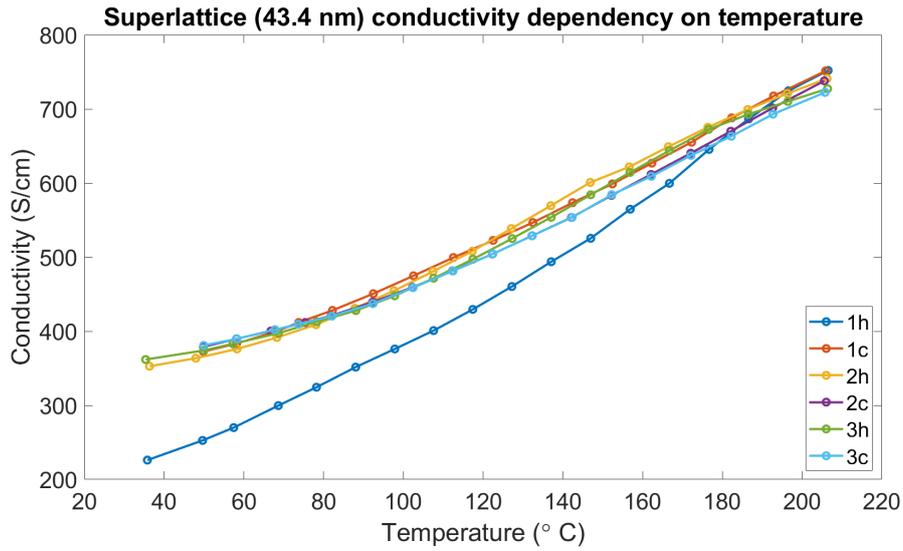
Similarly, electrical conductivity of GeTe/Sb₂Te₃ superlattice-like film that is slightly thicker, with pulse number ratio between GeTe and Sb₂Te₃ of 2, increases with increasing temperature, as shown in Figure 8a, using four-point probe method. For this medium thickness, the sample in four-point probe measurement was measured after two-point probe measurement, shown in Figure 8b, consequently without any electrodes deposited on to the superlattice-like film. As a result, it is plausible to expect that the superlattice-like film electrical conductivity would for this thickness to be similar between the two methods. It was observed that the electrical conductivity measured in four-point probe measurement, shown in Figure 8a, is lower than the result from two-point probe measurement, shown in Figure 8b. This again shows that four-point probe measurement gives lower electrical conductivity than two-point probe measurement.

For the thickest superlattice-like film with pulse number ratio between GeTe and Sb₂Te₃ of 4, there are two different samples measured in four-point probe measurement, namely the fresh and old sample, denoted by Fresh and Old in Figure 9a. In this measurement, electrodes composed of Au and Ti were deposited onto both fresh and old sample. Similar to the medium thickness superlattice-like film, the old sample in the four-point probe measurement is the sample that was used after the third cycle of the two probe measurements. During the placing of the fresh sample, there is some residual silver glue on the side of the films which greatly influenced the results from four-point probe measurement. To overcome this, the side where the excess silver glue resided had been cleaved by diamond knife to make sure that no currents would flow to the silver glue.

From Figure 9a, electrical conductivity of the thickest superlattice-like film increases after first cycle heating. This was observed in both samples, although this increment is greater in fresh sample which is five times as much as the electrical conductivity increment after first heating cycle in the old sample. $\Delta\sigma$ in the old sample during the heating cycle is found to be 100 S/cm in a close agreement with found in two-point probe measurement during third heating cycle which is around 150 S/cm.



(a)

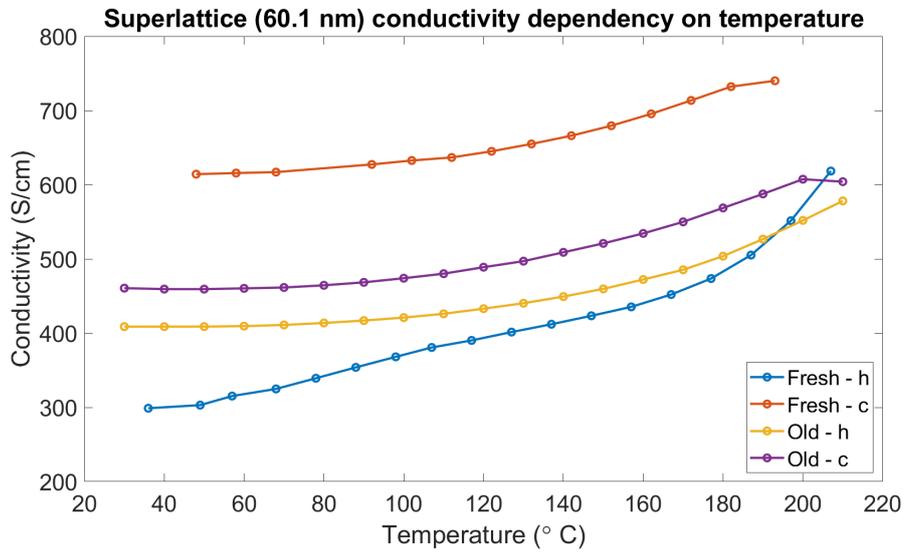


(b)

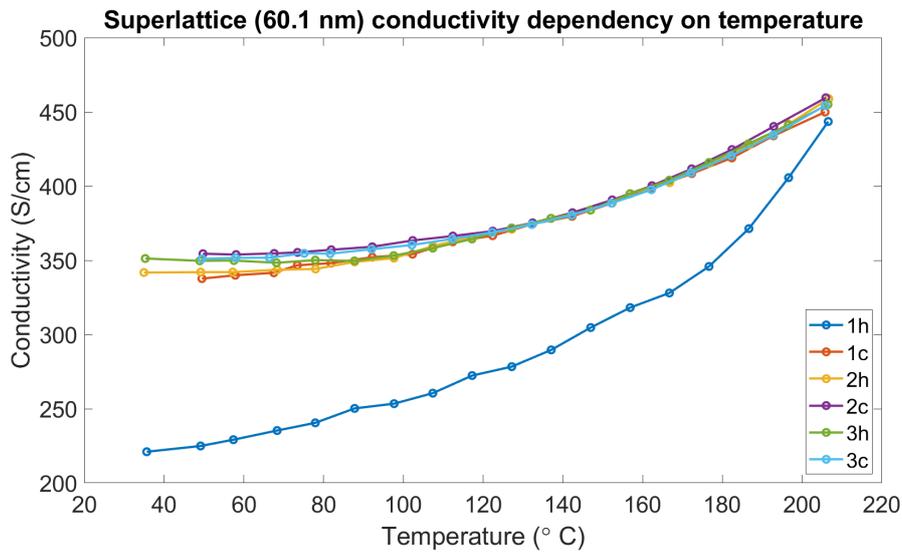
Figure 8: Dependency on temperature of the medium superlattice-like films electrical conductivity measured in three cycles using four-point (a) and two-point probe method (b).

However, when comparing the fresh heating cycle in four-point probe measurement, $\Delta\sigma$ is found to be almost 300 S/cm, exceeding the value of the first heating cycle from the other method. At room and high temperature, the electrical conductivity of GeTe/Sb₂Te₃ superlattice-like film from four-point probe measurement is also higher than the results from two-point probe measurement. The presence of elec-

trodes really improve the results of four-point probe measurement and overcome the cooling problem observed in measurements without electrodes.



(a)



(b)

Figure 9: Dependency on temperature of the thickest superlattice-like films electrical conductivity measured in three cycles using four-point (a) and two-point probe method (b).

4.3 Discussion

The different thicknesses of superlattice-like films also result in different electrical conductivity but this relationship cannot be found easily as only one sample has been measured for three cycles. When considering only one cycle measurement, the closest approximation to the relationship between electrical conductivity and thickness of the sample is that the different electrical conductivity at room and high temperature, $\Delta\sigma$, is higher for smaller thickness. This is confirmed by two probes measurement and in accordance to the solution of van der Pauw equation that the conductivity is inversely proportional to the thickness of the films.

The phenomena of increasing electrical conductivity after first heating, observed in all three samples, is suspected due to intermixing or diffusion between interfaces of GeTe and Sb_2Te_3 (7). It is then important to look more into diffusivity of GeTe and Sb_2Te_3 interface in superlattice-like films to understand the superlattice-like films electrical conductivity as whole that seems to be dependent on the thickness of their constituent layers. In this case, assuming the thickness of the constituent layers of the thinnest superlattice-like films to be the same, Sb_2Te_3 and GeTe layers might have been diffused completely whereas in thicker films, diffusion only occur in the interface between Sb_2Te_3 and GeTe. Hence by quantifying the diffusivity/intermixing of the superlattice-like films at different thicknesses, the domination of each constituent layer could be determined and optimization of superlattice-like film electrical conductivity could be done.

The thickness of Sb_2Te_3 in superlattice can also be varied to understand completely the conductivity once the superlattice is intermixed/diffused. On top of that, this also allows for optimization of the thickness between the Sb_2Te_3 and GeTe layers within the superlattice-like films. It has been observed already that the thickness of Sb_2Te_3 and GeTe single layer is different even when deposited in the same way. Therefore, it will be useful to conduct imaging measurement before and after measurement to see how the thickness of superlattice-like films changes after being intermixed/diffused.

Another way to optimize superlattice-like thermoelectric properties is by considering their semiconducting behaviour. While GeTe is a widely common p-type semiconductor, Sb_2Te_3 in a superlattice structure is more versatile in such a way its conducting properties can be controlled. In order to increase the electrical conductivity of superlattice-like films, to further increase the figure of merit, Sb_2Te_3 can be tuned to a n-type semiconductor. Theoretically, the junction between GeTe and Sb_2Te_3 in the superlattice-like films will then create a depletion region, where there

are not any charge carriers. This region has a definite width and will get smaller when a forward bias is applied. When this occurs, the films would then have more conductivity, as more charge carriers are allowed to diffuse over two junctions.

It is still plausible to expect that thicker GeTe layers in the superlattice-like films would give more electrical conductivity shift after first heating cycle, which could be due to incomplete diffusion in thicker GeTe layer, as shown in Figure 7b, 8b, 9b. From those results, the electrical conductivity of superlattice-like films at room temperature changes after first heating cycle. Nevertheless, although this jump in electrical conductivity is similar to that of single layer GeTe, transport measurement such as van der Pauw and Seebeck method cannot be singly used to fully reveal the mechanism behind the diffusivity in the constituent layers of GeTe/Sb₂Te₃ superlattice-like films.

The main issue using van der Pauw technique is contact issue. With electrodes there might be some capacitance issues that was also observed in experiment and without electrodes, the probes would leave holes on the sample. To overcome the contact issue, it is always better to have electrodes where it is placed not to close to the edge of the sample and the electrodes have to be noticeable or not too small. This would decrease the error in probe displacement, leading to more reliable results as the current would flow the same amount of distance between electrodes. Not only electrical contact, thermal contact is also an important parameter that would influence the result as the sample needs to be heated up uniformly and cooled down properly. The cooling part is a little bit trickier to create since it requires a good cooling system, which might not always come from a good thermal contact.

Although there were some differences in the experimental setup and procedures, for example whether the heat contact is iron plate or only silver glue or whether electrodes were used as electrical contacts or not, the only consideration before taking measurement is the contact resistance. This procedure requires contact resistance to be similar between the two points where current is run through. If the difference is significant, the probe height needs to be adjusted until the requirement is met. This comes at the expense of having the contact at different heights which indeed gives different contact resistance. It is still important that the four probes create the same geometry as the sample.

5 Conclusions

The single layer of Sb_2Te_3 shows a metallic behaviour that the resistivity is proportional to temperature whereas GeTe shows a semiconducting behaviour. These have been confirmed using van der Pauw and Seebeck method. For both layers, the conductivity is found to be smaller in van der Pauw method than Seebeck method which comes from the addition of contact resistance.

It has been observed that GeTe/ Sb_2Te_3 superlattice-like film has a low resistivity, $16.67 \mu\Omega m$ once intermixing occurred. Electrical conductivity of superlattice like films is dominated by GeTe layers when GeTe layers is increased. This has been observed as the electrical conductivity after first heating cycle increases, resembles the phase change properties of GeTe. This higher and stable electrical conductivity occurs due to intermixing/diffusion of Sb_2Te_3 and GeTe layers in the superlattice-like films which depends on their consequent layers thickness. Therefore, atomic structure images of each sample needs to be taken before and after measurement in order to investigate thickness evolution upon intermixing in superlattice-like films.

Optimization of superlattice-like films can be done in several ways. Firstly, a more deep and thorough understanding of intermixing/diffusion between each sample within the superlattice-like films. This can be quantified by studying their consequent layers thickness evolution using imaging measurement. Secondly, the best Sb_2Te_3 to GeTe ratio of thickness can be found by varying the thickness of Sb_2Te_3 layers. Lastly, only a n-type Sb_2Te_3 deposited to allow conductivity optimization.

Although there is contact issue that needs to be resolved using electrodes, van der Pauw method is still a robust technique to measure sheet resistance, especially for thin films. This is due to the fact that it is easy to check whether if there are any problems with the setup. In the same sense it is quite intuitive to improve the result from this measurement. However, its cannot be used as the only tool to understand electrical transport in superlattice-like structure.

References

- [1] M. E. Ellion, “Combined photovoltaic-thermoelectric solar cell and solar cell array,” Dec. 1 1987, uS Patent 4,710,588.
- [2] C. B. Vining, “An inconvenient truth about thermoelectrics,” *Nature materials*, vol. 8, no. 2, pp. 83–85, 2009.
- [3] T. Harman, P. Taylor, M. Walsh, and B. LaForge, “Quantum dot superlattice thermoelectric materials and devices,” *science*, vol. 297, no. 5590, pp. 2229–2232, 2002.
- [4] R. Venkatasubramanian, E. Siivola, T. Colpitts, and B. O’quinn, “Thin-film thermoelectric devices with high room-temperature figures of merit,” *Nature*, vol. 413, no. 6856, pp. 597–602, 2001.
- [5] M. Eschbach, E. Młyńczak, J. Kellner, J. Kampmeier, M. Lanius, E. Neumann, C. Weyrich, M. Gehlmann, P. Gospodarič, S. Döring *et al.*, “Realization of a vertical topological p–n junction in epitaxial sb 2 te 3/bi 2 te 3 heterostructures,” *Nature communications*, vol. 6, no. 1, pp. 1–7, 2015.
- [6] R. Simpson, P. Fons, A. Kolobov, T. Fukaya, M. Krbal, T. Yagi, and J. Tomimaga, “Interfacial phase-change memory,” *Nature nanotechnology*, vol. 6, no. 8, pp. 501–505, 2011.
- [7] J. Momand, R. Wang, J. E. Boschker, M. A. Verheijen, R. Calarco, and B. J. Kooi, “Interface formation of two-and three-dimensionally bonded materials in the case of gete–sb 2 te 3 superlattices,” *Nanoscale*, vol. 7, no. 45, pp. 19 136–19 143, 2015.
- [8] R. Hein, J. Gibson, R. Mazelsky, R. Miller, and J. Hulm, “Superconductivity in germanium telluride,” *Physical Review Letters*, vol. 12, no. 12, p. 320, 1964.
- [9] Z. Liu, J. Mao, T.-H. Liu, G. Chen, and Z. Ren, “Nano-microstructural control of phonon engineering for thermoelectric energy harvesting,” *MRS Bulletin*, vol. 43, no. 3, pp. 181–186, 2018.
- [10] B. Poudel, Q. Hao, Y. Ma, Y. Lan, A. Minnich, B. Yu, X. Yan, D. Wang, A. Muto, D. Vashaee *et al.*, “High-thermoelectric performance of nanostructured bismuth antimony telluride bulk alloys,” *Science*, vol. 320, no. 5876, pp. 634–638, 2008.

- [11] T. J. Seebeck, *Ueber den Magnetismus der galvanischen Kette*, 1822.
- [12] J. Banaszczyk, A. Schwarz, G. De Mey, and L. Van Langenhove, “The van der pauw method for sheet resistance measurements of polypyrrole-coated paraaramide woven fabrics,” *Journal of Applied Polymer Science*, vol. 117, no. 5, pp. 2553–2558, 2010.
- [13] N. Peranio, M. Winkler, D. Bessas, Z. Aabdin, J. König, H. Böttner, R. Hermann, and O. Eibl, “Room-temperature mbe deposition, thermoelectric properties, and advanced structural characterization of binary bi2te3 and sb2te3 thin films,” *Journal of alloys and compounds*, vol. 521, pp. 163–173, 2012.
- [14] M.-Y. Kim and T.-S. Oh, “Thermoelectric thin film device of cross-plane configuration processed by electrodeposition and flip-chip bonding,” *Materials Transactions*, p. M2012265, 2012.
- [15] H. Zou, D. Rowe, and S. Williams, “Peltier effect in a co-evaporated sb2te3 (p)-bi2te3 (n) thin film thermocouple,” *Thin Solid Films*, vol. 408, no. 1-2, pp. 270–274, 2002.
- [16] F. Ping, Z. Zhuang-Hao, L. Guang-Xing, C. Xing-Min, and Z. Dong-Ping, “Composition-dependent characterization of sb2te3 thin films prepared by ion beam sputtering deposition,” *Chinese Physics Letters*, vol. 27, no. 8, p. 087201, 2010.
- [17] S. Zastrow, J. Gooth, T. Boehnert, S. Heiderich, W. Toellner, S. Heimann, S. Schulz, and K. Nielsch, “Thermoelectric transport and hall measurements of low defect sb2te3 thin films grown by atomic layer deposition,” *Semiconductor science and technology*, vol. 28, no. 3, p. 035010, 2013.
- [18] S. Bahl and K. Chopra, “Amorphous versus crystalline gete films. iii. electrical properties and band structure,” *Journal of Applied Physics*, vol. 41, no. 5, pp. 2196–2212, 1970.
- [19] T. Sarnet, T. Hatanpaa, E. Puukilainen, M. Mattinen, M. Vehkamaki, K. Mizohata, M. Ritala, and M. Leskela, “Atomic layer deposition and characterization of bi2te3 thin films,” *The Journal of Physical Chemistry A*, vol. 119, no. 11, pp. 2298–2306, 2015.

- [20] T. Siegrist, P. Jost, H. Volker, M. Woda, P. Merkelbach, C. Schlockermann, and M. Wuttig, “Disorder-induced localization in crystalline phase-change materials,” *Nature materials*, vol. 10, no. 3, pp. 202–208, 2011.
- [21] X. Sun, E. Thelander, J. W. Gerlach, U. Decker, and B. Rauschenbach, “Crystallization kinetics of geTe phase-change thin films grown by pulsed laser deposition,” *Journal of Physics D: Applied Physics*, vol. 48, no. 29, p. 295304, 2015.
- [22] Z. Li, N. Miao, J. Zhou, Z. Sun, Z. Liu, and H. Xu, “High thermoelectric performance of few-quintuple Sb₂Te₃ nanofilms,” *Nano Energy*, vol. 43, pp. 285–290, 2018.
- [23] L. Goncalves, P. Alpuim, A. G. Rolo, and J. Correia, “Thermal co-evaporation of Sb₂Te₃ thin-films optimized for thermoelectric applications,” *Thin Solid Films*, vol. 519, no. 13, pp. 4152–4157, 2011.

A Appendix

A.1 Sheet Resistance

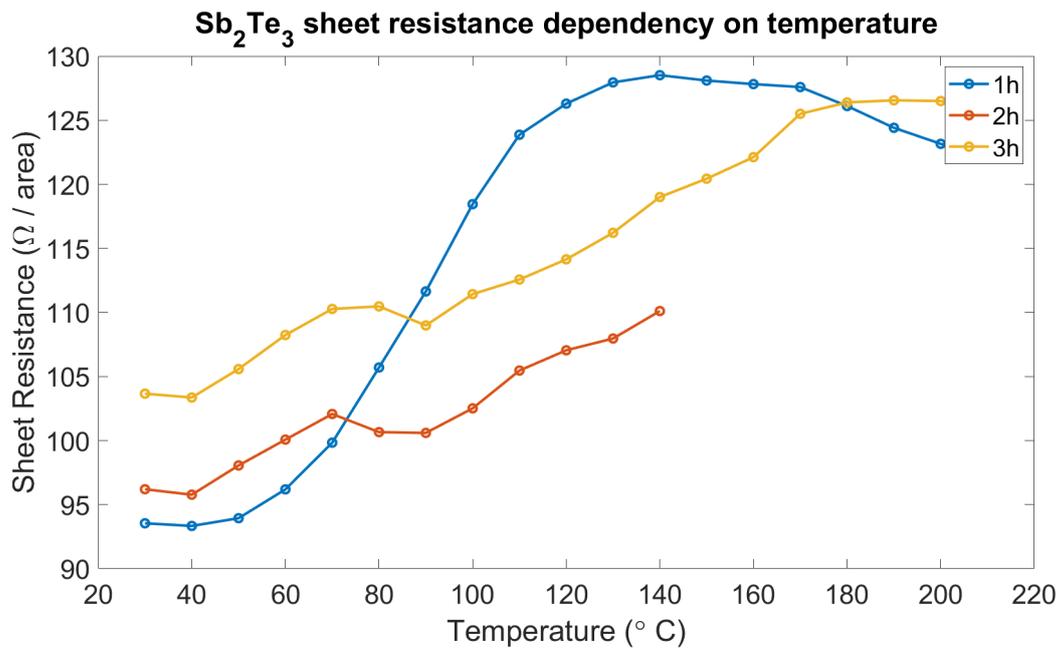


Figure A.1: Sheet resistance dependency on temperature for Sb₂Te₃ single layer.

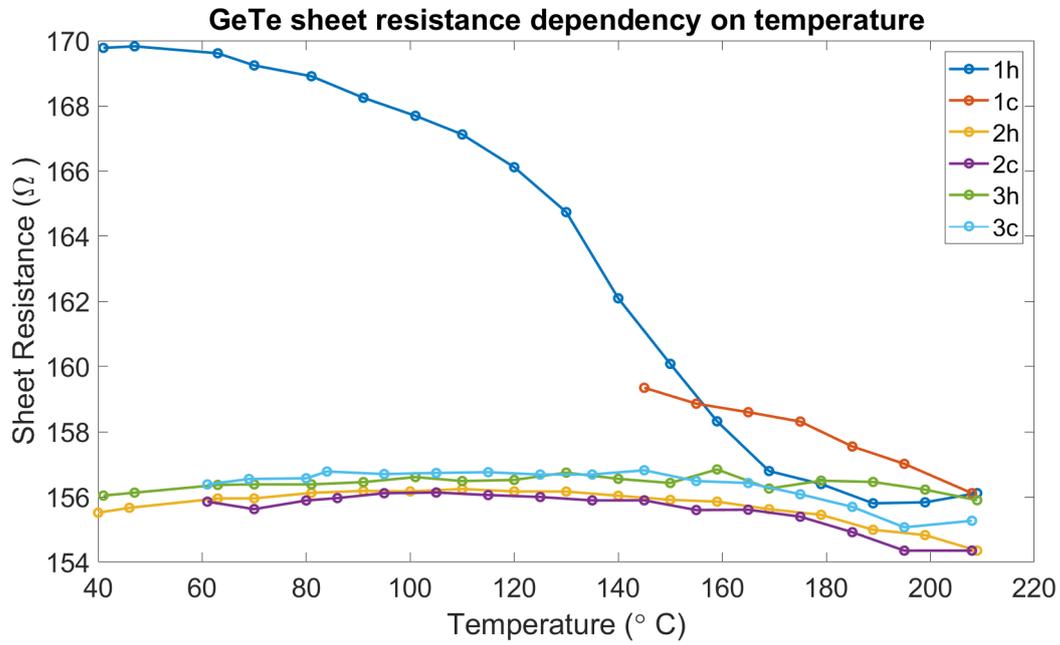


Figure A.2: Sheet resistance dependency on temperature for GeTe single layer.

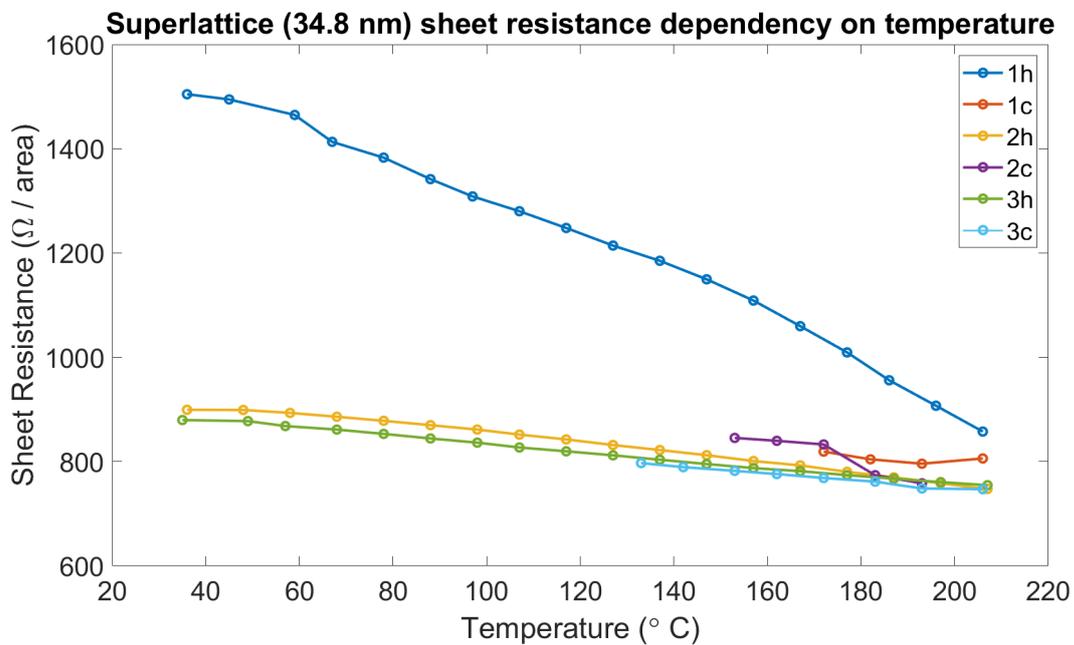


Figure A.3: Sheet resistance dependency on temperature for the thinnest superlattice-like films of GeTe/Sb₂Te₃.

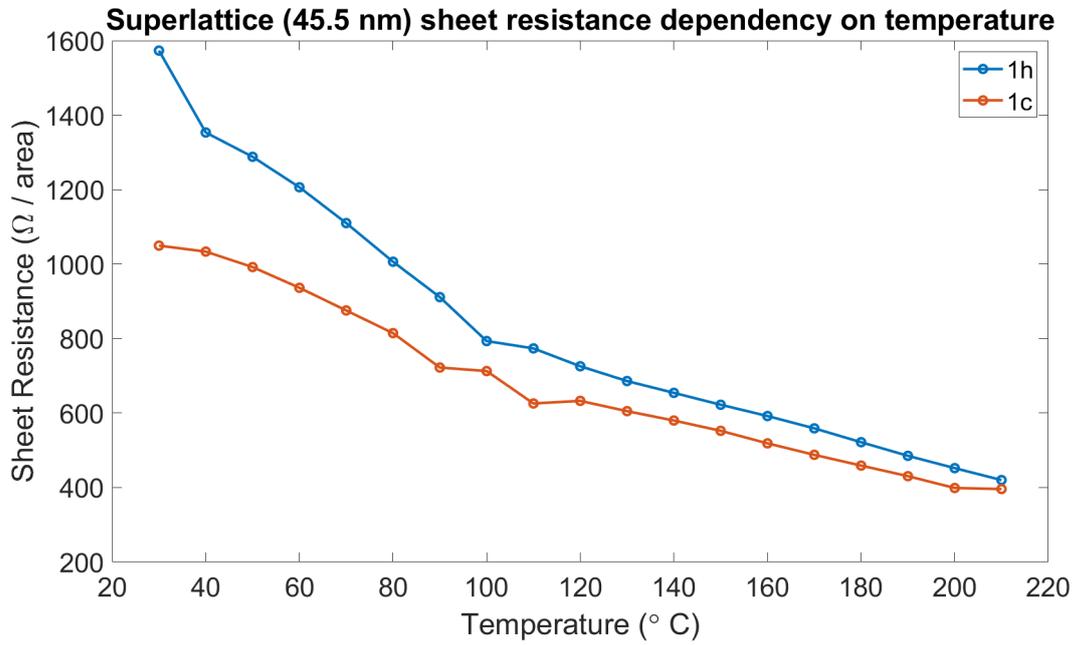


Figure A.4: Sheet resistance dependency on temperature for the medium superlattice-like films of GeTe/Sb₂Te₃.

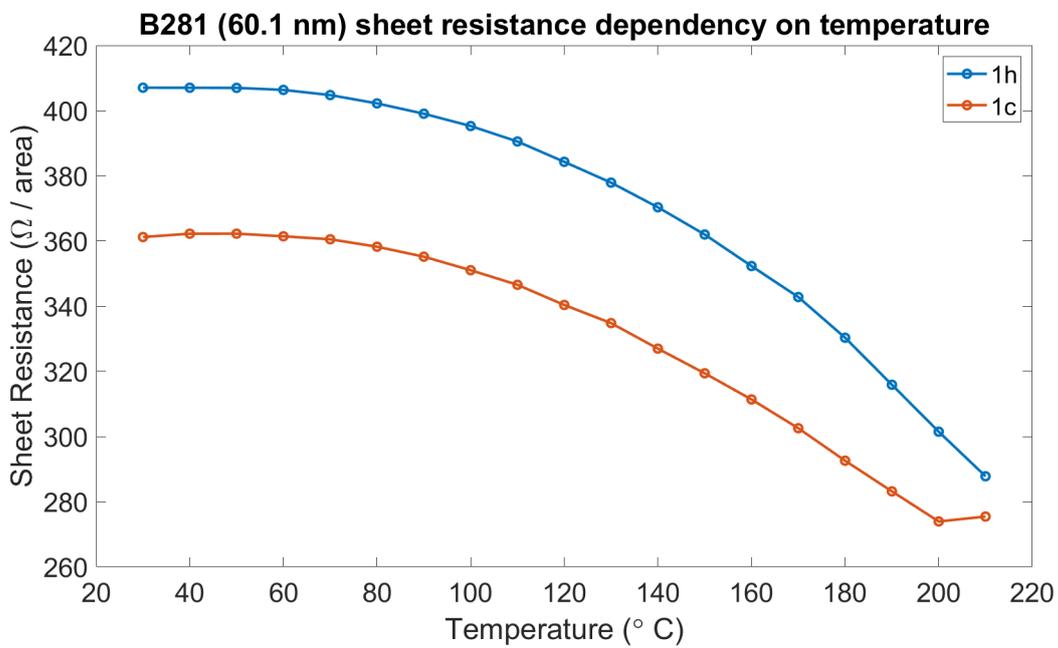


Figure A.5: Sheet resistance dependency on temperature for the thickest superlattice-like films of GeTe/Sb₂Te₃, old sample.

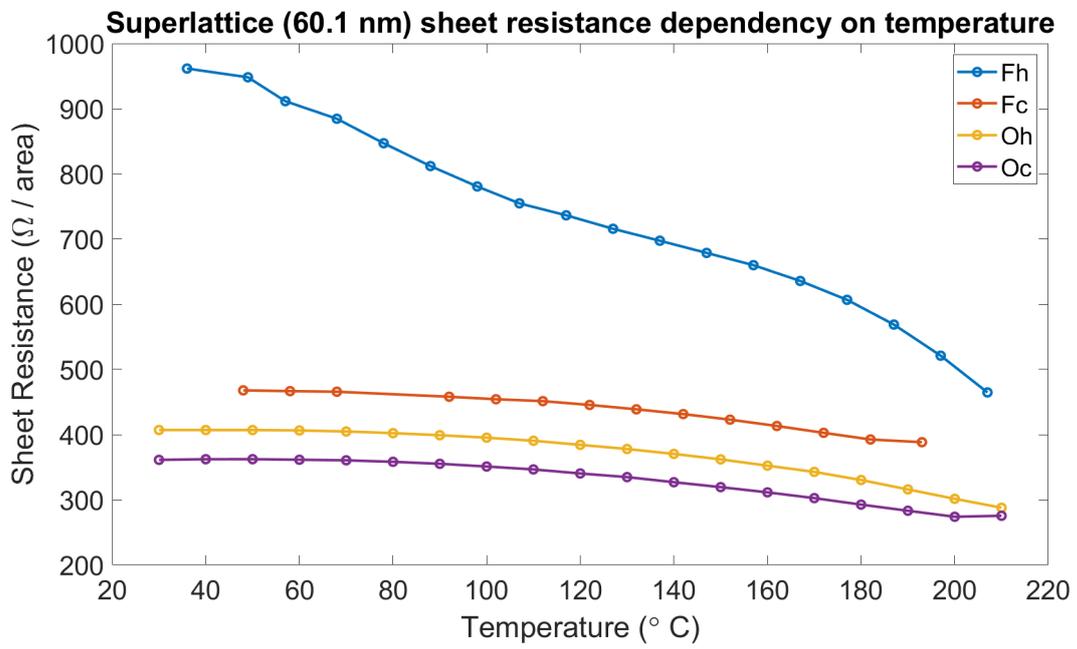


Figure A.6: Sheet resistance dependency on temperature for the thinnest superlattice-like films of GeTe/Sb₂Te₃, fresh sample.