Relationship between statistical shift of the Fermi level and activation energy of conductivity in phase-change materials

Y V Vorobyov1,*, A V Ermachikhin1 and E P Trusov1

1 Ryazan State Radio Engineering University, Ryazan 390005, Russia

* vorobjov.y.v@rsreu.ru

Abstract. The non-Arrhenius behaviour of conductivity of phase-change materials is analysed in terms of the statistical shift of Fermi level. To show this connection, a simplified model for the density of states in a phase-change material is proposed to simulate the temperature dependence of the Fermi level. Comparison of the temperature dependence of conductivity of Ge2Sb2Te5 with the simulation results allowed estimating the position of defect levels in the bandgap.

1. Introduction

Phase-change memory (PCM) is one of the modern non-volatile memory technologies. It is based on reversible phase transitions of an active material between its crystalline and non-crystalline phase. The PCM combines high storage density with high throughput, which makes it one of the best candidates for Storage Class Memory paradigm.

One of the main advantages of PCM technology is an exceptionally high electrical contrast between two phases of an active material, reaching several orders of magnitude[1]. This allows multilevel storage by partial conversion of material in a memory cell from one phase state to another [2]. However, the closer adjacent resistance levels are the more prone to error the readout scheme becomes, limiting the amount of information stored in a memory cell. In practice, however, it is not the only limitation. Non-crystalline materials are unstable in nature and tend to change their properties over time. In particular, the resistivity of phase-change materials in non-crystalline phase increases with time and its phenomenon is called “resistance drift” in literature[3]. It is commonly attributed to the structural relaxation[4,5], which leads to gradual changes of electronic structure of material, impacting its electrical properties.

Temperature dependence of conductivity in phase-change materials resembles Arrhenius behaviour with the value of activation energy $E_\sigma$ typically about half of the bandgap value. Taking into account the so-called pinning of the Fermi level in amorphous semiconductors [6] near midgap, the value of $E_\sigma$ can be related to the position of Fermi level. However, it is true only in the limit of temperature independent Fermi level position, which leads to strictly linear Arrhenius plot for conductivity[7]. For phase-change materials, it is rarely the case. What this implies is that the deviations of conductivity from the strictly Arrhenius behaviour could be utilized to obtain information about temperature dependent Fermi level position [8].

The aim of the current work is to connect the statistical shift of Fermi level with the experimentally observed temperature dependence of conductivity in phase-change materials.
2. Statistical shift of Fermi level
The statistical shift of the Fermi level is calculated on the basis of equilibrium occupancy of allowed states in the energetic spectrum of a typical chalcogenide semiconductor. Assuming equilibrium conditions, we neglect the influence of current flow through the material, which accompanies measurement of many electro-physical characteristics, including conductivity. Our assumption implies, therefore, that the magnitude of current is small enough not to perturb the equilibrium conditions significantly, i.e. Fermi levels for electrons and holes coincide [9]. Since the phase-change materials considered here are typically low-conductive, the current density is very low, and the aforementioned assumption of equilibrium is satisfied.

2.1. Model DoS function
We assume that the DoS distribution includes the common features of non-crystalline semiconductors: allowed bands tailing into the bandgap, as well as deep bands due to defects situated close to the midgap.

Band tails are the consequence of non-crystalline nature of considered materials: absence of long-range order smears edges of allowed bands[10]. Fluctuations of the short-range order, such as bond length and angle distortions, participate in band tailing as well [6]. Although states in band tails formally belong to the corresponding band, electrons occupying these states are localized meaning that each of them is confined nearby a specific point of space and is not able to move freely. Localized states in the tails are separated from extended states in the conduction band (CB) and valence band (VB) by sharp mobility edges $E_C$ and $E_V$, which in the current context define band edges, and, accordingly, the bandgap $E_g = E_C - E_V$.

For the band tails, exponential form is commonly assumed [11], which can be shown to fit optical absorption spectra very well [12]. Therefore, we define

$$g^c(E) = g_0^c \exp\left(\frac{E - E_c}{\gamma_c}\right),$$

$$g^v(E) = g_0^v \exp\left(\frac{E_v - E}{\gamma_v}\right),$$

where $\gamma_c$ and $\gamma_v$ define the breadth of the band tails.

Deep states in the bandgap correspond to point defects of atomic structure of material [13]. They appear because topological disorder in non-crystalline solids leads to a large number of “wrong” bonds, resulting from atoms having non-optimal coordinations [14]. Therefore, under- and overcoordinated atoms are presented in non-crystalline solids in significant extent. Because many phase-change materials are multicomponent compounds, the chemical disorder contributes as well to the formation of point defects. Density of such defects could reach $10^{19}$–$10^{20} \text{cm}^{-3}$ for certain cases [6]. The model of charged dangling bond [6,14] suggests that such structural defects could be singly or doubly occupied by a charge carrier. Taking into account electronic correlations [15], two energy levels should be assigned to such a defect on a single-particle DoS picture. We denote them $E_A$ and $E_B$, meaning their acceptor-like (neutral when empty) or donor-like (neutral when occupied) behaviour. Due to disorder, the energy of a specific defect type could vary [16]. That is why the electronic states, corresponding to defects in non-crystalline solids, should be treated as bands rather than discrete levels.

We assume Gaussian shape of DoS distribution, corresponding to the defect bands:

$$g^A(E) = 2 \sqrt{\frac{\ln 2 N_A}{\pi \epsilon_A}} \exp\left[-\frac{4 \ln 2}{\epsilon_A} \left(\frac{E - E_A}{\epsilon_A}\right)^2\right],$$
\[ g^D(E) = 2 \sqrt{\frac{\ln 2 N_D}{\pi \epsilon_D}} \exp \left[ -4 \ln 2 \left( \frac{E - E_D}{\epsilon_D} \right)^2 \right], \]  
(4)

where \( N_A \) and \( N_D \) — defect densities, \( \epsilon_A \) and \( \epsilon_D \) — full width at half maximum of defect bands, \( E_A \) and \( E_D \) — positions of defect bands with respect to some reference energy level. Below, the VB edge \( E_V \) is this reference level.

It is known, that the bandgap \( E_g \) in semiconductors decreases considerably with increasing material temperature. We use the data from [17–19] together with the model proposed by Cody et al.[20] to simulate the temperature dependence of \( E_g \) in Ge\(_2\)Sb\(_2\)Te\(_5\):

\[ E_g(T) = E_0 - \frac{K}{\exp \left( \frac{\Theta_E}{T} \right) - 1}, \]  
(5)

where \( E_0 = 0.941 \) eV, \( K = 0.138 \) eV, and \( \Theta_E = 214 \) K are material parameters, determined using least-square minimization of the data reported in [17–19].

Shportko[19] has demonstrated that the Urbach energy \( E_U \), defined as the breadth of exponential tail on the optical absorption curve, is inversely proportional to \( E_g \) in Ge\(_2\)Sb\(_2\)Te\(_5\). This is again in line with the model proposed by Cody et al.[20]:

\[ E_U = \frac{k_B \Theta_E}{\sigma_U \left( 1 + X \right) - \frac{1}{K} (E_g - E_0)}, \]  
(6)

where \( X \) is a measure of structural disorder, and \( \sigma_U \) — Urbach tail parameter. According to [19], for Ge\(_2\)Sb\(_2\)Te\(_5\) one could use \( X = 9.13 \), and \( \sigma_U = 1.49 \).

According to empirical analysis of O’Leary et al.[12,21], \( E_U \) is a measure of tailing of the Joint DoS function, defined as the convolution of VB DoS with CB DoS. The value of \( E_U \) in such context could be defined as \( E_U^n = \gamma_C^n + \gamma_V^n \), where \( n \) is about 4–5. According to the published data [22,23], \( \gamma_V \) is about 30 meV at room temperature, which together with the value of \( E_U \) allows to define \( \gamma_C \) as well. For the temperature dependence of tail widths, it seems possible to apply the linear scaling in the following way:

\[ \gamma_C(T) = \beta_C E_U(T), \]  
(7)

\[ \gamma_V(T) = \beta_V E_U(T), \]  
(8)

where \( \beta_C \) and \( \beta_V \) are temperature independent constants.

On the basis of comparison of numerical simulation results with the data of thermopower of Ge\(_2\)Sb\(_2\)Te\(_5\), authors of [24] proposed linear dependence for the scaling of defect bands positions:

\[ E_0^A(T) = \alpha_A E_g(T), \]  
(9)

\[ E_0^D(T) = \alpha_D E_g(T), \]  
(10)

where \( \alpha_A \) and \( \alpha_D \) are temperature independent constants. The same concept of linear “stretching” of DoS picture was proposed in [25] to explain the results of conductivity measurements after aging of GeTe, which is accompanied by an increase of activation energy for conductivity. It should be noted, that authors of [24,25] did not include variations of band tails into their model.

2.2. Calculation of Fermi level position

Once the DoS picture is defined, one can calculate the equilibrium Fermi level position from the condition of charge neutrality:

\[ p_0 - n_0 + p_t - n_t + q_D - q_A = 0, \]  
(11)
where \( p_0, n_0 \) — densities of free holes and electrons, \( p_t, n_t \) — densities of holes and electrons trapped in the states of band tails, and \( q_D, q_A \) — density of ionized donor and acceptor defects.

As the Fermi level is supposed to be effectively pinned near midgap due to high density of charged defects, free carriers concentrations are given for the non-degenerate case:

\[
\begin{align*}
n_0 &= N_C \exp \left( \frac{E_F - E_C}{k_B T} \right) = N_C e^{-\frac{E_D}{k_B T} x}, \\
p_0 &= N_V \exp \left( \frac{E_V - E_F}{k_B T} \right) = N_V x^{-1},
\end{align*}
\]

where \( N_C, N_V \) — effective density of states in allowed bands, and

\[ x = \exp \left( \frac{E_{ VC}}{k_B T} \right). \]

For the electrons, trapped in the conductance band tail, we may write:

\[
n_t = \int_{-\infty}^{E_C} g^C(E) f_n(E) dE,
\]

where \( g^C(E) \) is given by (1), and \( f_n(E) \) is the occupation function for the CB tail. The choice of the lower integration bound \( E = -\infty \) instead of \( E = E_V \) facilitates integration and is justified by the rapidly vanishing band tail density. The following form of the occupation function is assumed:

\[
f_n(E) = \frac{1}{1 + g \exp \left( \frac{E - E_F}{k_B T} \right)},
\]

where \( g = 1 \) is taken for tail states. After a formal integration of (15) taking into account (1) and (16) we obtain:

\[
n_t = g^C_0 \gamma_C \frac{E_C}{\gamma_C} \left( \frac{k_B T}{\gamma_C}; 1 + \frac{k_B T}{\gamma_C}; -e^{\frac{E_D}{k_B T} x^{-1}} \right),
\]

where \( F(a, b; c; z) \) — hypergeometric function. In analogous manner, for the holes trapped in the VB tail states:

\[
p_t = g^V_0 \gamma_V F \left( \frac{k_B T}{\gamma_V}; 1 + \frac{k_B T}{\gamma_V}; -x \right),
\]

where the following form of occupation function was assumed (taking \( g = 1 \)):

\[
f_p(E) = \frac{1}{1 + g \exp \left( \frac{E_F - E_V}{k_B T} \right)},
\]

The density of ionized donors is found integrating their distribution (4) over the bandgap:

\[
q_D = 2 \sqrt{\frac{\ln 2 N_D}{\pi \epsilon_D}} \int_{E_V}^{E_C} \exp \left[ -4 \ln 2 \left( \frac{E - E_D}{\epsilon_D} \right)^2 \right] \left[ 1 - f_n(E) \right] dE,
\]

where \( g = 1/2 \) is taken calculating \( f_n(E) \). For ionized acceptors, the integration is analogous:
\[ q_A = 2 \sqrt{\frac{\ln 2 N_A}{\pi \varepsilon_A}} E_C \int_{E_V}^{E_C} \exp \left[ -4 \ln 2 \left( \frac{E - E_A}{\varepsilon_A} \right)^2 \right] \left[ 1 - f_p(E) \right] dE. \] (21)

Unfortunately, the integrals in (20) and (21) cannot be represented in closed form. One should instead rely on numerical integration methods. Due to rapid decrease of Gaussian function, we use narrower integration interval \((-2.5\varepsilon; +2.5\varepsilon)\) to speed up the convergence of numerical integration.

Having all terms of neutrality equation (11) defined as functions of \(x\) (14), one could obtain the value of \(x\) using a numerical root finding method. Analytic solution for \(E_F\) is only possible for simple cases [26].

3. Results and discussion

To compare the results of simulation with the behaviour of an actual phase-change material, we performed measurements of conductivity of Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} thin film. Further details regarding samples preparation and experimental setup could be found in previous work [27]. The temperature dependence of Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} conductivity is presented in figure 1 in the Arrhenius coordinate system. Linear approximation of this plot gives the value of activation energy \(E_\sigma = 391\) meV.

![Figure 1. Temperature dependence of Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} conductivity.](image)

From the simple band transport theory, assuming predominant conduction by free holes in the considered material[28], we obtain:

\[ \sigma = q\mu_h N_v \exp \left( -\frac{E_F - E_V}{k_B T} \right), \] (22)

where \(\mu_h\) is the holes mobility. The multiplier before exponent is known as the microscopic prefactor for conductivity\(\sigma_0\). Within the standard band transport model, it takes values about 100–600 S/cm for an amorphous semiconductor[29] and could be considered temperature independent. Thus, we can estimate the Fermi level temperature dependence \(E_F - E_V = k_B T \ln(\sigma_0/\sigma)\), making assumption regarding a value of \(\sigma_0\). The results are presented in figure 2 for several possible values of \(\sigma_0\). For each of assumed prefactor value, \(E_F\) remains below the midgap, justifying the use of (22). Solid lines are derived from the experiment data in figure 1, and squares are results of approximation of experimental data by the model presented in the previous section. It should be stressed here, that all the curves in figure 2 are derived from the same conductivity data. In other words, no unique value of the Fermi level position could be derived from the conductivity data, and usual assumption \(E_\sigma = E_F - E_V\) is not correct in the general case of temperature-dependent Fermi level. It is interesting to note that the value of \(E_\sigma = 0.391\) eV, determined from the linear fit of the data in figure 1, is very close to the Fermi level position, corresponding to the assumed prefactor value between 500 and 600 S/cm (figure 2).
This is due to the fact, that $E_F$ is practically temperature independent there, which is the only condition when $E_\sigma = E_F - E_V$ holds.

To simplify the model, we assume equal band parameters, namely $N_C = N_V = N_{\text{eff}}$ and $g_0^C = g_0^V = g_0$. The numbers of deep donors and acceptors are also considered equal, $N_A = N_D = N$, due to the specific mechanism of their formation\[30\]. Under such assumptions, the charge neutrality equation does not depend explicitly on the values of $N_C(N_V)$, $g_0^C(g_0^V)$, and $N_D(N_A)$, but rather on their relative values. What this means is that we can treat one of those three parameters fixed—change of its value will result merely in rescaling of other two without disturbing the quality of approximation. Following [23], we assume $N_{\text{eff}}$ fixed and equal to $3.9 \times 10^{21}$ cm$^{-3}$. The widths of donor and acceptor bands are also considered fixed and equal 25 meV for both bands. Change of this value results in a slight parallel shift of the whole picture of temperature dependence of $E_F$. Therefore, there are 4 adjustable parameters in our model: number of deep defects $N$, DoS at the edge of allowed bands $g_0$, and positions of donor and acceptor bands $E_D$ and $E_A$ at some reference temperature (300 K herein).

Approximation results depicted by squares in figure 2 demonstrate, that the quality of approximation does not depend on the assumed value of microscopic prefactor, forbidding determination of the latter by comparison of the simulation results with the experimental data. From the other side, the extent to which different approximation parameters depend on the assumed value of microscopic prefactor varies considerably (figure 3).
As one can see from figure 3(a), uncertainty of the prefactor value produces relatively small variation of $E_D$ and $E_A$. It leads us to conclusion, that positions of defect bands are not very sensitive to the assumed prefactor value. According to the presented analysis, deep donors and acceptors are located about 0.25 eV and 0.58 eV above VB. We could compare those results with the values $E_D = 0.26$ eV and $E_A = 0.41$ eV reported in [23] for the GeTe compound on the basis of modulated photocurrent method (MPC). Both Ge$_2$Sb$_2$Te$_5$ and GeTe exhibit similar MPC behaviour [17], which is related to the same mechanism of defects formation in those materials involving different bonding configurations of Ge atoms [31]. The results for $E_D$ are in excellent agreement, however, the difference between values for $E_A$ is significant, which could be related to different compositions of materials. Another difference between our results is that authors of [23] obtained 2–3 orders of magnitude higher value of density of states in band tails. If the same band tail states density were assumed in our model, we should have compensated for its increase by proportional addition of deep states to obtain the same value of $E_F$, because of neutrality condition. However, the value of $N$ in our simulation is already high, reaching $10^{22}$ cm$^{-3}$ (figure 3(b)). Taking into account the density of atoms in amorphous Ge$_2$Sb$_2$Te$_5$, which is about $3 \cdot 10^{22}$ cm$^{-3}$ [32], further increase of $N$ by 2–3 orders of magnitude seems physically unrealistic.

In contrast to the values of $E_D$ and $E_A$, parameters $N$ and $g_0$ exhibit orders of magnitude change over the assumed range of microscopic prefactor values. Therefore, the experimental data on conductivity alone is not enough to extract reliable values of these DoS parameters. It seems possible to extract their values, supporting presented analysis with the data on temperature dependence of other material parameters, such as thermopower and mobility, or with the results of other DoS measurement techniques.

4. Conclusion
The experimental data on conductivity in phase-change materials is commonly used to merely obtain the single value of activation energy. In the present work we show how the conductivity of Ge$_2$Sb$_2$Te$_5$ is related to the position of Fermi level and its temperature dependence. Unfortunately, using conductivity data alone it is impossible to determine the position of Fermi level without taking the assumption regarding the value of the conductivity prefactor. Without a priori known value of the prefactor, the extracted Fermi level position, corresponding to a given temperature dependence of conductivity, is not unique. Because of that one should not interpret the value of activation energy for conductivity as the Fermi level position.

Performing analysis of temperature dependence of conductivity within a simplified model for DoS distribution and assuming extended states conduction, we were able to estimate specific parameters of DoS distribution. Despite the exact value of the conductivity prefactor is not known, the positions of deep donors and acceptors are not particularly sensitive to its assumed value, thus providing definite degree of certainty to the analysis. The temperature dependence of conductivity can, therefore, provide deeper insights into the underlying physics of phase-change materials, than it is commonly utilized.

Acknowledgments
The work is supported by Russian Science Foundation under project no. 19-73-00150. Experiments were performed using facilities of Regional Centre for Probe Microscopy of RSREU.

References
[1] Friedrich I, Weidenhof V, Njoroge W, Franz P and Wuttig M 2000 Structural transformations of Ge$_2$Sb$_2$Te$_5$ films studied by electrical resistance measurements J. Appl. Phys. 87 4130–4
[2] Athmanathan A, Stanisavljevic M, Cheon J, Kang S, Ahn C, Yoon J, Shin M, Kim T, Papandreou N, Pozidis H and Eleftheriou E 2015 A 6-bit drift-resilient readout scheme for multi-level phase-change memory Proc. 2014 IEEE Asian Solid-State Circuits Conf. A-SSCC 2014 137–40
[3] Pirovano A, Lacaita A L, Pellizzer F, Kostylev S A, Benvenuti A and Bez R 2004 Low-field
amorphous state resistance and threshold voltage drift in chalcogenide materials IEEE Trans. Electron Devices 51 714–9

[4] Noé P, Sabbione C, Castellani N, Veu G, Navarro G, Sousa V, Hippert F and D’Acapito F 2015 Structural change with the resistance drift phenomenon in amorphous GeTe phase change materials’ thin films J. Phys. D. Appl. Phys. 49 035305

[5] Zhang W and Ma E 2020 Unveiling the structural origin to control resistance drift in phase-change memory materials Mater. Today 41 156–76

[6] Elliott S R 1983 Physics of amorphous materials (New York: Longman Inc.)

[7] Fritzsch H 1971 Optical and electrical energy gaps in amorphous semiconductors J. Non. Cryst. Solids 6 49–76

[8] Vorobyov Y, Ermachikhin A, Yakubov A, Trusov E, Fedyanina M, Lazarenko P and Kozyukhin S 2021 Temperature activated conductivity of Ge2Sb2Te5: connection to the variation of Fermi level and implications on resistance drift J. Phys. D: Appl. Phys. https://doi.org/10.1088/1361-6463/abfe7e

[9] Blakemore J S 1962 Semiconductor statistics (Oxford: Pergamon Press Ltd.)

[10] Gubanov A I 1965 Quantum Electron Theory of Amorphous Conductors (Boston, MA: Springer US)

[11] Adler D 1987 Theory of Amorphous Semiconductors Key Eng. Mater. 13–15 11–7

[12] O’Leary S K, Johnson S R and Lim P K 1997 The relationship between the distribution of electronic states and the optical absorption spectrum of an amorphous semiconductor: An empirical analysis J. Appl. Phys. 82 3334–40

[13] Adler D 1980 Theory of amorphous semiconductors Sol. Cells 2 199–226

[14] Adler D 1985 Chemistry and Physics of Covalent Amorphous Semiconductors Physical Properties of Amorphous Materials ed. D Adler, B B Schwartz and M C Steele (Boston, MA: Springer US) pp 5–103

[15] Yoffa E J, Rodrigues W A and Adler D 1979 Electronic correlations in narrow-band solids Phys. Rev. B 19 1203–12

[16] Street R A 1976 Luminescence in amorphous semiconductors Adv. Phys. 25 397–453

[17] Luckas J, Kremers S, Krebs D, Salinga M, Wuttig M and Longeaud C 2011 The influence of a temperature dependent bandgap on the energy scale of modulated photocurrent experiments J. Appl. Phys. 110 013719

[18] Rütten M, Kaes M, Albert A, Wuttig M and Salinga M 2015 Relation between bandgap and resistance drift in amorphous phase change materials Sci. Rep. 5 17362

[19] Shportko K V 2019 Disorder and compositional dependences in Urbach-Martienssen tails in amorphous (GeTe)x(Sb2Te3)1−x alloys Sci. Rep. 9 6030

[20] Cody G D, Tiedje T, Abeles B, Brooks B and Goldstein Y 1981 Disorder and the Optical-Absorption Edge of Hydrogenated Amorphous Silicon Phys. Rev. Lett. 47 1480–3

[21] O’Leary S K 2004 An analytical density of states and joint density of states analysis of amorphous semiconductors J. Appl. Phys. 96 3680–6

[22] Rütten M, Geilen A, Sebastian A, Krebs D and Salinga M 2019 Localised states and their capture characteristics in amorphous phase-change materials Sci. Rep. 9 6592

[23] Longeaud C, Luckas J, Krebs D, Carius R, Kломфасс J and Wuttig M 2012 On the density of states of germanium telluride J. Appl. Phys. 112 113714

[24] Kaes M and Salinga M 2016 Impact of defect occupation on conduction in amorphous Ge2Sb2Te5 Sci. Rep. 6 31699

[25] Krebs D, Bachmann T, Jonnalagadda P, Dellmann L and Raoux S 2014 Changes in electrical transport and density of states of phase change materials upon resistance drift New J. Phys. 16 043015

[26] Vorobyov Y, Avachev A, Tolkach N, Ermachikhin A and Kusakin D 2017 An analytical solution for the Fermi level of the non-degenerate semiconductor in thermal equilibrium over a wide temperature range 2017 6th Mediterranean Conference on Embedded Computing
[27] Vorobyov Y V, Yakubov A O and Ermachikhin A V 2020 Temperature dependence of Ge$_2$Sb$_2$Te$_5$ conductivity and its change during aging *IOP Conf. Ser. Mater. Sci. Eng.* **889** 012032

[28] Nardone M, Simon M, Karpov I V and Karpov V G 2012 Electrical conduction in chalcogenide glasses of phase change memory *J. Appl. Phys.* **112** 071101

[29] Mott N F and Davis E A 1979 *Electronic Processes in Non-crystalline Materials* (Oxford University Press)

[30] Mott N F, Davis E A and Street R A 1975 States in the gap and recombination in amorphous semiconductors *Philos. Mag.* **32** 961–96

[31] Konstantinou K, Mocanu F C, Lee T H and Elliott S R 2019 Revealing the intrinsic nature of the mid-gap defects in amorphous Ge$_2$Sb$_2$Te$_5$ *Nat. Commun.* **10** 3065

[32] Nonaka T, Ohbayashi G, Toriumi Y, Mori Y and Hashimoto H 2000 Crystal structure of GeTe and Ge$_2$Sb$_2$Te$_5$ meta-stable phase *Thin Solid Films* **370** 258–61