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Some results on the germanium telluride density of states

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Abstract. Germanium telluride (GeTe) is one of the most studied phase change materials. Surprisingly, only little is known about the distribution of states (DOS) in its band gap. In this paper we investigate both experimentally and theoretically the amorphous GeTe DOS and we propose a model for this DOS as well as orders of magnitude of some of the transport parameters of this material. The DOS we propose is subsequently compared to those suggested to explain the threshold switching and the resistance drift phenomena.

1. Introduction

Phase change materials (PCM) exhibit amazing properties that make them excellent candidates for rewritable data storage. Though already included in everyday devices, improving their potentialities is still a matter of research. Intense studies aim at data storage using multiple resistance levels created by different amorphous volumes within phase change memory devices. However, it was observed that drift of these resistance levels may eventually lead to a loss of information if they come too close. Some theories propose that this drift originates from an evolution with time of the density of states (DOS) of the PCM band gap [1, 2]. Another phenomenon is still a matter of debate: the threshold switching and the drift of the threshold voltage. Again the models proposed are based on the DOS of the PCM band gap [3] and on its evolution with time or annealing of the material [4].

Germanium telluride (GeTe) is one of the most studied PCM but the states distribution in its band gap remains speculative. In its amorphous state (a-GeTe) most authors agree on the presence of band tail states but their extent in the gap is only roughly estimated. Additionally, deeper states may be present but their position in energy and distributions are unknown [5, 6]. To investigate the PCM density of states the modulated photocurrent technique (MPC) seems to be well adapted [7]. Indeed, we have recently probed the a-GeTe DOS by means of this technique [8] and shown that the ‘standard’ treatment of the MPC data [9, 10] should be modified in order to take into account the evolution of the band gap width with respect to temperature [11]. In this paper, we investigate the a-GeTe DOS both experimentally and by means of numerical calculations, trying to reproduce evolutions with temperature T of the dark and photo conductivity, of the MPC spectra and variations with photon energy of the absorption coefficient measured on this material.

After a brief description of the samples and the experiments we used to characterize them we present experimental results. We insist on the modulated photocurrent technique and show how it is possible to account for the widening of the a-GeTe band gap with decreasing temperature to derive a refined DOS spectroscopy. Then we use a numerical simulation to try to reproduce the experimental
results by a proper choice of transport parameters and DOS. We detail the method we used to estimate the extended states hole mobility $\mu_p$ and the equivalent density of states $N_v$ at the valence band edge $E_v$. From the results of these numerical calculations we propose a model for the a-GeTe DOS. We detail the different states distributions as well as their capture coefficients. From this model, we expect to get a better understanding of the DOS in a-GeTe and, further, to investigate on the possible link(s) between the respective evolutions of resistivity, threshold switching and DOS. We finally look at the agreements of this model of DOS with some models found in the literature.

2. Samples and experiments
GeTe amorphous thin films, 100-200 nm thick, were deposited on glass substrates by means of a LS 320 von Ardenne Sputter system operating in constant 20–25 W power mode, 20 s.c.c.m. Ar flow and with stoichiometric targets of 99.99 % purity. For Fourier Transform Infrared (FTIR) spectroscopy in reflectance mode the glass was covered with a 200 nm thick aluminium film before a-GeTe deposition. For electrical measurements two parallel rectangular Al ohmic electrodes of 8 mm length and 2 mm apart were deposited on top of the phase change films deposited on glass.

Steady-state dark and photo-conductivity (SSPC) were measured each 10 K on samples fitted onto the cold finger of a dynamically pumped cryostat for temperatures in the range 100-300 K. A constant flux ($F_{dc} = 10^{16}$ cm$^{-2}$s$^{-1}$) of infrared light (850 nm) was used for photoconductivity measurements. After reaching the measurement temperature under dark conditions, we waited 10 min for the temperature to stabilize and took the average value of 20 acquisitions, one each second, to extract the dark conductivity. Then the light was turned on and we waited one more minute under light before recording again 20 values, the average of which leads to the estimate of photoconductivity. The error was estimated to be less than 5 %. The same light source was used to perform MPC experiments to determine the DOS distribution in the band gap of these films. MPC measurements were achieved each 20 K or each 5 K for $100 \leq T \leq 300$ K. The amplitude of the modulated flux was 4 times lower than the mean dc flux and the modulation frequencies at a given temperature were in the range 12 Hz – 40 kHz. For each couple (temperature, frequency) the measured phase shift and modulus of the alternating current were the average of 20 acquisitions by a lock-in amplifier and the error could be estimated to be of the order of 10%. From FTIR measurements, we deduced the evolution of the band gap with $T$. Reflectance measurements were achieved for $4 \leq T \leq 300$ K with photon energies $E$ from 0.04 to 1 eV. The absorption coefficient $\alpha(E)$ was deduced from the analysis of the reflectance pattern by means of a Tauc-Lorentz oscillator model proposed by the software SCOUT [12]. The band gap was defined as the energy value for which $\alpha(E)=10^4$ cm$^{-1}$ known as the $E_{04}$. In addition, Seebeck measurements were performed from room temperature to 220 K giving the position of the Fermi level $E_F$ with respect to $E_v$. Finally, for some samples, photo-deflection spectroscopy (PDS) experiments [13, 14] were achieved at room temperature and the curves were calibrated with the absorption coefficient.

3. Experimental results
Figure 1 displays a typical Arrhenius plot of the dark conductivity and total conductivity under illumination -that we shall call photoconductivity in the following- of an a-GeTe film. These films presented very little difference between dark and photo current from 300 K down to 200 K. The dark conductivity at $T = 300$ K was of the order of $\sigma_{\text{d})} = 5\times10^4$ S/cm and, from the plot of figure 1 we deduced that $\sigma_{\text{dark}}$ had an activation energy $E_a \approx 0.31-0.32$ eV for $210 \leq T \leq 300$ K. For temperatures below 200 K the temperature variations of the dark conductivity clearly depart from a straight line and this departure may be interpreted as the onset of a hopping conduction as we shall see latter.

Figure 2 displays a PDS spectrum normalized to the absorption coefficient for which three zones can be observed. At low energy the absorption coefficient varies exponentially with energy and we can define an Urbach energy $E_u$ of the order of 63 meV. This linear variation is followed by a parabolic variation and, further, by a saturation when all the photons are absorbed by the layer.

Although the samples were not highly photoconductive over a large range of temperature, it was possible to perform MPC experiments from 300 K down to 100 K. It was shown [9, 10] that from the
measurement of the modulus of the photoconductivity \( |\sigma_{ac}| \), resulting from modulated generation rate \( G_{ac} \), and of \( \phi \), its phase shift referred to the excitation, it is possible to achieve a DOS spectroscopy deducing the variations with energy of the quantity \( NC_p/\mu_p \), \( N \) being the density of states at an energy \( E_\omega \) and \( C_p \) the capture coefficient of the states trapping free carriers (holes in a-GeTe, hence the index \( p \)), from the equations

\[
\frac{N(E_\omega)C_p}{\mu_p} = \frac{2}{\pi k_B T} q G_{ac} \sin \phi \left| \sigma_{ac} \right| \tag{1}
\]

with

\[
E_\omega - E_v = k_B T \ln \left( \frac{C_p N_v}{\omega} \right) \tag{2}
\]

\( k_B \) being the Boltzmann constant, \( \omega \) the angular frequency of the modulation and \( q \) the electron charge.

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{fig1.png}
\caption{Typical variations with \( T \) of dark and photo conductivities observed on an a-GeTe film.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{fig2.png}
\caption{Typical PDS spectrum normalized to the absorption coefficient observed on the a-GeTe films (symbols). The vertical lines define three zones: an exponential variation (left), a parabolic variation (middle) and a saturation of the absorption coefficient (right).}
\end{figure}

The reader may note that all the quantities on the right hand side of Eq. (1) are known. Therefore, by varying experimentally \( T \) and \( \omega \), Eqs. (1)-(2) offer the possibility to scan the DOS of the material provided \( C_p, \mu_p \) and \( N_v \) are known. One quantity of particular importance is the attempt to escape frequency \( \nu = C_p N_v \) for it fixes the energy scale of the DOS spectroscopy (see Eq. (2)).

The symbols of figure 3 display a first scan of the density of states of an a-GeTe film. Each symbol corresponds to a given temperature and, at this temperature, the deepest symbol in energy corresponds to the lower frequency (12 Hz) and the highest to the higher frequency (40 kHz). For this plot the attempt to escape frequency was fixed at \( \nu = 10^{12} \text{ s}^{-1} \). The upper envelope of these symbols describes a DOS made of deep states and of a valence band tail (VBT). It can be seen that all the sets of symbols fit onto this envelope for the points obtained at high frequency and depart from it for the points obtained at low frequency. The choice of \( \nu \) was not done at random but precisely to obtain this behaviour. Indeed, it was shown [10] that the departure of the points from the upper envelope could be due to the influence of the mean dc flux needed to achieve the modulation. This mean dc flux gives rise to a recombination zone in the gap, the extent in energy of which depends on its intensity: the larger the flux, the larger the extent. Eq. (1) being valid only for trapping states, when applied to
Experimental data controlled by the recombination region, the deepest states probed at a given temperature, it leads to this departure from the upper envelope that describes the trapping states outside the recombination region. The estimate of $\nu$ was done in order to have the upper points of a spectrum obtained at a given $T$ matching with the upper points of a spectrum obtained at the nearest temperatures at least for the VBT states. For lower values of $\nu$ the spectra would cross one another and for higher values they would not match at all. This procedure is one of the possibilities to estimate the $\nu$ values that are appropriate to describe the valence band tail states.

As far as deep states are concerned it can be seen that MPC spectra reveal a bump around 0.4 eV. A better investigation of this bump was achieved by varying the temperature in 5 K steps for $225 \leq T \leq 250$ K. The spectra are plotted by full lines in figure 1 for two different values of $\nu$: $10^{12}$ s$^{-1}$ for the spectra on the right hand side of figure 3 and $2.5 \times 10^8$ s$^{-1}$ for the spectra on the left hand side. To have a clear overview, the $NC/\mu$ values for these spectra have been divided by 8 as shown in the figure. A well defined bell shape is described by the different spectra. In addition, with $\nu = 2.5 \times 10^8$ s$^{-1}$ the maxima of the spectra are located at the same energy which is not the case with $\nu = 10^{12}$ s$^{-1}$ as indicated by the short full line segments. Obviously, if this bell shape distribution corresponds to a peak of states its maximum must stay at the same energy position independently of the experimental temperature. This suggests that the proper $\nu$ associated to these states is of the order of $10^8$ s$^{-1}$ and it is a wrong value of $\nu$ used in Eq. (2) that leads to the distribution of deep states described by symbols around 0.4 eV in the first scan we made of the DOS. The alignment of the maxima of several MPC spectra is another possibility to estimate the attempt to escape frequency of the probed states [15].

The two procedures described above to find estimates of $\nu$ can be refined if one takes into account the fact that the band gap of a-GeTe varies with temperature. Indeed, FTIR measurements at different temperatures showed that the a-GeTe band gap varies with $T$ following the equation

$$E_{0d}(T) = E_{0d}(T=0 K) - \xi T^2$$

(3)

$\xi$ being of the order of $\xi \approx 1.3 \times 10^{-6}$ eV/K$^2$. It means that between 300 K and 100 K the gap width increases by 0.1 eV, a rather large value. In addition, Seebeck measurements showed that this evolution of the gap was essentially due to a movement of the valence band edge toward a fixed conduction band edge. Therefore, Eq. (2) has to and can be corrected to take account of the gap shift with $T$. Two types of corrections can be proposed and are detailed in Ref. 11. To correct the MPC energy scaling given by Eq. (2), and to define the same energy origin for all the MPC spectra taking account that the conduction band edge does not move with temperature in agreement with the Seebeck measurements, we may consider that the shrinkage of the gap results in a modification of the trap energies proportional to their positions at 0 K, i.e. states near the valence band edge shift by the full correction term $-\xi T^2$, mid-gap states only by $-0.5 \xi T^2$ and the energy positions of the states close to the conduction
band are almost unchanged. In this case the correction is made pro rata to the energy position of the traps and one has

$$\Delta E = k_B T \ln \left( \frac{\nu}{\nu_0} \right) - \xi T^2 \left( 1 - \frac{\Delta E}{E_{\text{opt}}} \right)$$

(4)

giving

$$\Delta E = \frac{k_B T \ln \left( \frac{\nu}{\nu_0} \right) - \xi T^2}{1 - \xi T^2 / E_{\text{opt}}}$$

(5)

that leads to the spectra displayed in figure 4.

$$\nu = 10^{12} \text{ s}^{-1}$$

Figure 4. NC/µ distributions of states taking account of a pro rata correction to the spectra displayed in figure 3.

It can be seen in figure 4 that the VBT is still well described using $\nu = 10^{12} \text{ s}^{-1}$ all the parts of the spectra obtained at high frequency fitting well from one spectrum to the other. However, for temperatures below 140 K the spectra clearly depart from the upper envelope as if the mean dc flux used to perform the experiment was too high and a wide recombination region was needed to reach equilibrium conditions. This possibility has to be considered but the VBT increasing exponentially the recombination zone created by the mean dc flux does not need to extend widely to create enough recombining states. The reader may also note that the disagreement of the spectra with the upper envelope increases with decreasing temperature. The reason of this increasing disagreement has to be probably found in an increasing influence of the hopping conduction with decreasing temperature. Indeed, we have shown that hopping conduction could be responsible for such departures of the MPC spectra from the upper envelope [16]. We would like to underline that the temperature range in which hopping seems to have a large influence on the MPC spectra, say below 160 K, corresponds to the temperature range for which dark conductivity is not following anymore an activated behaviour in the Arrhenius plot of the dark conductivity (See figure 1).

As far as deep states are concerned the bell shape distribution is still present but we had to increase the $\nu$ value up to $\nu = 10^{10} \text{ s}^{-1}$ to align the maxima of the different spectra at the same energy of $\approx 0.24$ eV. For the deepest states (0.5 eV above $E_v$) we lack information to estimate the $\nu$ value, for none of the procedures described above seem to be applicable in this case. That is why the MPC spectra have been plotted with the same $\nu$ as for the VBT states though the true value is probably different.

To investigate more precisely on this distribution of states we have developed a numerical calculation that can be used to reproduce the experimental results. The basic idea of this approach is not to reproduce the experimental data point after point but rather to underline the main trends observed experimentally.
4. Numerical calculation

The numerical calculation that we have developed can reproduce the behaviours of many techniques among which the SSPC, the MPC and the variation with photon energy of the absorption coefficient. The program, DeOSSt, is available on the web site of the LGEP [17]. The material parameters (band gap width, mobilities, gap states distribution, capture coefficients, etc.) and the ‘experimental’ parameters (temperature, flux, frequency of the modulation,…) can be defined by the user. The program calculates the data corresponding to the chosen experiment and these data can be treated as ‘experimental’ results subsequently and compared with real experimental results. The number of adjustable parameters is rather large. Therefore, one may introduce as many experimental data as possible to minimize the number of unknowns. For instance one can introduce the band gap width, choose the valence band tail width, fix the Fermi level position, or some \( \nu \) values from the experimental data. The other parameters are adjustable in order to eventually reproduce the general experimental trends observed in SSPC, MPC and PDS but these adjustments cannot be achieved randomly since we have to fit the results of three independent experiments.

From the SSPC measurements we deduce an order of magnitude of the dark Fermi level position above the valence band edge from the activation energy of dark conductivity \( E_f - E_v \approx 0.31 \text{ eV} \). Considering an expression of the conductivity \( \sigma \) is

\[
\sigma = q\mu_p N_v \exp\left[-\frac{(E_f - E_v)}{k_B T}\right]
\]

we can deduce a good order of magnitude of the product \( \mu_p N_v \) at room temperature using also the \( \sigma \) value at 300 K, \( \sigma = 5 \times 10^4 \text{ S/cm} \), to finally end with \( \mu_p N_v \approx 10^{31} \text{ cm}^{-1}\text{V}^{-1}\text{s}^{-1} \). We can combine these results with those of the MPC experiment. This technique reveals a valence band tail decreasing exponentially from the valence band edge following the equation

\[
N(E) = N(E_v)\exp\left[-\frac{(E_v - E)}{E_{v_{bt}}}\right]
\]

We can then deduce an order of magnitude of the characteristic energy of the VBT, \( E_{v_{bt}} \approx 30-33 \text{ meV} \). The best matching we have for the different MPC spectra describing the VBT is given by \( \nu = C_p N_v = 10^{12} \text{ s}^{-1} \), from which we deduce an estimate of the ratio \( C_p/\mu_p \approx 10^9 \text{ cm/V} \). The estimate of \( NC/\mu \) from Eq. (1) is completely determined by experimental data. For instance, if we consider the data obtained for \( E - E_v = 0.2 \text{ eV} \), \( NC/\mu \approx 5 \times 10^{11} \text{ cm}^{-2}\text{V}^{-1}\text{eV}^{-1}\text{V} \), it is possible to estimate \( N(E_f) \approx 2 \times 10^{23} \text{ cm}^{-3}\text{eV}^{-1} \) from Eq. (7) assuming \( E_{v_{bt}} \approx 33 \text{ meV} \). Finally, if we suppose that \( N_v \approx k_B T N(E_f) \), we end with \( N_v \approx 5 \times 10^{21} \text{ cm}^{-3} \), \( \mu_p \approx 0.2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) and \( C_p \approx 2 \times 10^{10} \text{ cm}^3\text{s}^{-1} \).

The PDS spectrum is also a help for the determination of the DOS distribution. Indeed, in the photon energy range 0.5-0.8 eV the variations of the absorption coefficient describe an Urbach tail with a characteristic energy of 63 meV. Since the absorption coefficient can be defined as the convolution product of all the transitions from full states below the Fermi level toward empty states above it, it means that, assuming that the conduction band tail (CBT) is also varying exponentially, the characteristic energy of the CBT is much larger than that of the VBT, and of the order of 60 meV.

Nevertheless, the DOS distribution does not consist only in band tails for, if it was the case, the dark Fermi level would be pinned at their intersection, i. e. 0.25 eV above \( E_v \) as shown by the calculation. This value is too small to account for the experimental activation energy and, in addition, MPC has revealed deep states distributions among which a peak of states around 0.25 eV. This peak of states is most probably of donor type since acceptor states would push the Fermi level toward the valence band edge. It is well described by the MPC spectra with an attempt to escape frequency of \( \nu = 10^{10} \text{ s}^{-1} \), that is a capture coefficient of the order of \( C_p \approx 2 \times 10^{12} \text{ cm}^{-3}\text{s}^{-1} \) and from the \( NC/\mu \) value we can deduce \( N_{max} \approx 10^{22} \text{ cm}^3\text{eV}^{-1} \).

Figure 5(a) displays a first draft of a DOS that can be drawn from the experimental results. The band gap width has been set at 0.75 eV to obtain a good match between the calculated and
experimental PDS spectra. Figure 5(b) displays the MPC spectra that can be calculated from the DOS introduced in the numerical calculation. The valence band tail and the bump around 0.4 eV are well reproduced but the deepest states found experimentally above 0.4 eV are not reproduced by the calculation.

![Graph](image1)

**Figure 5.** (a) density of states deduced from the experiments the vertical line indicates the position of the dark Fermi level (b) MPC spectra calculated from the DOS displayed in (a).

Hence, this DOS does not bring satisfying results. In addition, the calculation showed that the dark Fermi level is not fixed and moves to different positions when the temperature varies, the result being a dark conductivity with an activation energy of 0.27 eV. Deeper states have to be added to fix the dark Fermi level position and give a contribution to the MPC spectra above say 0.45 eV.

The only way to reproduce a contribution of a DOS distribution to the MPC spectra for energies above 0.45 eV is to add at least one peak of states above the Fermi level. These states must be of acceptor type otherwise the Fermi level will move up toward the conduction band. The determination of their parameters (density and capture cross-section) is rather difficult because being located above the dark Fermi level and close to it they will not be pure trapping states as they can play a role in the recombination of carriers. They may give a contribution to the MPC data but for such states the application of Eq. (1) is theoretically not possible since it applies only to trapping states. Nevertheless, as we have done experimentally we can apply Eq.(1) to the calculated data and play with the parameters of these states to eventually get a result as close to the experiment as possible.

![Graph](image2)

**Figure 6.** (a) Density of states introduced into the numerical calculation. The dark Fermi level position is indicated by the vertical line. (b) MPC spectra obtained from the DOS in (a) plotted with $\nu = 10^{12}$ s$^{-1}$ (symbols) and with $\nu = 10^{10}$ s$^{-1}$ (lines). Same temperatures, same symbols and colors as figure 4.
Actually, to extend the MPC spectra towards high energy (deepest states) we had to add two distributions of acceptor states above the dark Fermi level. Figures 6(a) and 6(b) display the DOS introduced in the calculation and the corresponding MPC spectra, calculated for the same temperature as the experimental ones, respectively. The similarity between figure 6(b) and figure 4 is rather good though we have not reproduced the deepest states observed experimentally for energies of 0.55 eV and above. For this purpose we should have introduced more states above the Fermi level but, considering the lack of information concerning them, it would have been very speculative.

Figure 7. (a) Plot of dark and photo conductivity, experimental and calculated with the DOS of figures 6(a). (b) Plot of the absorption spectra, experimental (symbols), calculated with only the band tails (full line) and including the deep states (dashed line).

With such a distribution of states we can also reproduce variations of the photoconductivity on the whole range of investigated temperatures and those of dark conductivity for \( T \geq 210 \) K (See figure 7(a)), the disagreement at low temperatures originating from the fact that our calculation does not take hopping transport into account. We have also reproduced the PDS spectrum (See figure 7(b)). For this purpose we have chosen different values for the optical matrix elements \( C_{opt} \) of the band tails and the deep states. Taking only the band tails into account, with a VBT extent of 33 meV and a CBT extent of 60 meV and \( C_{opt} \approx 8 \times 10^{-22} \) cm\(^{-5/2}\)eV, leads to the full line curve matching the PDS spectrum in figure 7(b). We could not choose the same optical elements for the deep states otherwise they would have given rise to a large bump around 0.6 eV. Choosing optical elements 40 times lower than for the band tails leads to the fit displayed by a dashed line in figure 7(b). Nevertheless, these values for the optical elements are only estimates from our calculation and should be confirmed experimentally.

Before concluding we would like to add a few words on the distributions of states that we propose.

5. Discussion

The reader may note that the band tails we propose are in contradiction with those suggested by Bahl and Chopra [5, 6] that had imagined a CBT narrower than the VBT. However, they stressed that their proposal was only schematic because of the lack of information at the time they wrote their communication. In addition, a-GeTe is p-type and if the band tail states were distributed as they proposed the Fermi level would be pushed toward the conduction band, leading to n-type material. The tail states distributions may vary slightly from one sample to the other but MPC experiment has always revealed a rather narrow valence band tail distribution and the PDS results suggest a large conduction band tail to account for the large Urbach edge.

Concerning the deep states, we have modelled them by essentially two distributions of states on each side of the dark Fermi level, donor states below \( E_F \) and acceptor states above. These states were chosen to be monovalent whereas multivalent states with negative correlation energy have been
proposed as for instance in the valence alternating pair (VAP) model [18]. However, this VAP model, proposed for lone pair semiconductors as chalcogenide materials, has been recently questioned in the case of tellurides such as Ge$_2$Sb$_2$Te$_5$ [19]. That is why we have preferred to model the density of deep states by monovalent states that are easier to handle and to understand, particularly in terms of recombination paths, and with which we can describe rather accurately the transport behaviours we have observed experimentally.

We would like to underline that the distribution of states we propose is rather close to the one proposed by Ielmini et al. [3] to explain the threshold switching phenomenon. These authors have suggested that the threshold switching phenomenon originates from the presence of two deep levels of states. Assuming that the electrons are the majority carriers, their description is that the deeper level is a reservoir that may fill the upper level, close to the band, if the applied field is high enough to lower the barrier between states of the deeper level and states of the upper one. Our model of DOS includes these possible two levels, one of the main differences being that the majority carriers would be holes in our case but the process could be exactly the same.

However, we have found that the a-GeTe DOS distribution includes a large valence band tail that is not taken into account in Ielmini’s model. Besides, experimental data suggests that hopping is predominant at low temperature. Our simulation cannot deal with hopping in the case where the states have different capture cross-sections since the calculation time can rapidly becomes too long, but we have made a test with the same capture cross section for all the states and we have reproduced the same trends as those observed experimentally. We are then convinced that hopping is present, masked at room temperature by multiple trapping transport but becomes significant say below 160 K. A large literature on hopping transport in band tails can be found in which the concept of transport level is salient. Under ‘normal’ conditions, low temperature and low field, this transport level is far from the band edge. However, it was demonstrated that the transport level in band tail can be pushed as close as 50 meV from the band if the field is large enough [20]. Playing with the equations proposed by Cleve et al. it is easy to find that, with the VBT we have found, a field of 200 kV/cm, a reasonable value for a threshold field, would push the Fermi level to 75 meV ($3k_B T$ at room temperature) above the valence band. Hopping in band tail and evolution of the transport level with the applied field could be then an alternative to the Ielmini’s model.

Another point that we can deal with is the resistance drift phenomenon. This behaviour is usually attributed to an evolution of the band gap and/or band gap states with aging. Our model can reproduce this behaviour easily. On the one hand, an opening of the band gap without a modification of the DOS, as suggested by Boniardi et al. [21] and Pirovano et al. [22] for Ge$_2$Sb$_2$Te$_5$, will lead to a decrease of conductivity since the Fermi level is pinned by the deep states, and on the other hand, a decrease (increase) of the acceptor (donor) states will move $E_f$ toward the conduction band resulting in conductivity decrease reproducing the resistance drift phenomenon.

This discussion shows that the DOS distribution we propose neither rejects nor validates one particular model or the other. The DOS we proposed seems to be slightly more refined that any of the models mentioned above, gathering them in a whole picture. We think that, based on this DOS, the existing models describing the threshold switching and the resistance drift phenomena could be refined or some alternative explanation may be proposed if needed. We have already started SSPC, PDS and MPC measurements on aged samples and the results of these experiments should be helpful for future understanding of the complete transport mechanisms in PCM materials.

6. Conclusion

We have investigated on the density of states and transport parameters of a-GeTe by means of three different experiments: dark and photo-conductivity, PDS and MPC. We have underlined that the ‘standard’ treatment of MPC had to be refined to account for the evolution of the band gap width with temperature, and suggested a new treatment of the MPC data. From the experimental results of these three techniques we have shown that some of the a-GeTe transport parameters could be deduced.
Introducing these parameters into a numerical simulation we have reproduced all the main trends of the three experiments with a model of DOS distribution made essentially of two band tails, one donor deep states below the Fermi level and acceptor deep states above the Fermi level.

We have compared the DOS we propose with some of the models of the literature and found that it does not contradict any of them, providing a more elaborate picture of the states distribution instead since the features of this DOS can explain the threshold switching and the resistance drift phenomena. Experimental investigations on the DOS of aged or annealed a-GeTe should provide, by comparison with the as deposited state, a better comprehension of these two puzzling characteristics of PCM materials [23].

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References
[1] Pirovano A et al. 2004 IEDM Tech. Dig. 51 714