Changes in electrical transport and density of states of phase change materials upon resistance drift

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\textbf{Abstract}

Phase-change memory technology has become more mature in recent years. But some fundamental problems linked to the electrical transport properties in the amorphous phase of phase-change materials still need to be solved. The increase of resistance over time, called resistance drift, for example, poses a major challenge for the implementation of multilevel storage, which will eventually be necessary to remain competitive in terms of high storage densities. To link structural properties with electrical transport, a broader knowledge of (i) changes in the density of states (DoS) upon structural relaxation and (ii) the influence of defects on electrical transport is required. In this paper, we present temperature-dependent conductivity and photo-conductivity measurements on the archetype phase change material GeTe. It is shown that trap-limited band transport at high temperatures (above 165 K) and variable range hopping at low temperatures are the predominating transport mechanism. Based on measurements of the temperature dependence of the optical band gap, modulated photo-conductivity and photo-thermal deflection spectroscopy, a DoS model for GeTe was proposed. Using this DoS, the temperature dependence of conductivity and photo-conductivity has been simulated. Our work shows how changes in the DoS (band gap and defect distributions) will affect the electrical transport before and after...
temperature-accelerated drift. The decrease in conductivity upon annealing can be explained entirely by an increase of the band gap by about 12%. However, low-temperature photo-conductivity measurements revealed that a change in the defect density may also play a role.

Keywords: phase change materials, electrical transport, resistance drift, density of states, conductivity, photo-conductivity, temperature dependence

1. Introduction

The discovery of materials that can rapidly transform between a low reflective amorphous and a high-reflective crystalline phase enabled the commercialization of rewriteable optical storage technology in the late 1980s and early 1990s [1]. These so-called phase-change materials also exhibit a large electrical contrast between these two phases [2, 3]. The ability to read and write information entirely by means of electrical signals, suggested the use of phase-change materials for non-volatile memory and storage applications [4]. In recent years, the technology has become mature, with several semiconductor manufacturers already producing phase-change memory chips [5–8]. However, to succeed as a new kind of cheap memory that can serve as bridge between fast, but volatile DRAM and slow but non-volatile FLASH memory, multi-level phase-change technology also needs to be developed to become competitive in terms of cost per bit [9]. The main challenge to writing multiple states into a single cell is the noise and drift behavior of the high-resistive amorphous phase. Written state distributions will exhibit a finite width due to noise and broaden over time because the amorphous resistance increases with time with a certain variability. This will eventually lead to a crossing of levels, and thus loss of the stored data [10].

The drift and the noise behavior have both been attributed to the large defect distributions within the amorphous phase that dominate the transport behavior [11–16]. In this study, we establish a link between the changes in the electrical resistance upon drift and changes in the electronic density of states (DoS). Using temperature-dependent conductivity and photo-conductivity measurements on the promising phase change material GeTe [17], we are able to confirm a quantitative picture for the DoS and to predict the changes in the DoS that lead to an increased resistance over the entire range of temperatures investigated.

2. Experimental

2.1. Sample preparation

Samples were prepared on thermally oxidized Si wafers with an oxide thickness of 500 nm. First, 50 nm thick tungsten electrodes were deposited via DC magnetron sputtering. Next, a sputter cleaning step removed any oxide layer that may potentially be present on the electrode. Then, a 100 nm GeTe film and a 10 nm SiO$_2$ capping layer were deposited in situ onto the patterned wafer via DC and RF magnetron sputtering, respectively. The composition of the sputtered GeTe film was cross-checked using Rutherford backscattering and found to be Ge (51 ± 0.5)Te(49 ± 0.5). After GeTe deposition, the electrodes were opened by removing the patterned resist in an acetone bath. In this way, exposure of the GeTe film to any temperature
above 300 K during fabrication, which could have accelerated drift, was prevented. The resulting lateral GeTe bridges between the electrodes had different absolute sizes and varying aspect ratios of width to length. The samples used for this study had an aspect ratio of 1501, electrodes with a meander structure and a pad size of 960 \( \mu m \times 2461 \mu m \).

2.2. Measurement setup

Conductivity and photo-conductivity measurements were done using a ST-500-2-UHT cryogenic probe station from Janis Research. Constant cooling in the vacuum chamber is provided by a liquid nitrogen flow through the copper sample mount. The sample temperature is heated by a 50 W resistive heater close to the surface of the chuck controlled by a LakeShore model 336 temperature controller. The temperature is measured at various places in the chamber with LakeShore DT-670B-CU-HT Si diodes to enable precise temperature control. Measuring the temperature at the sample surface, a maximum temperature measurement error of \( \pm 2.5 \) K was determined which resulted from the varying quality of the thermal contact between sample and chuck when re-mounting the sample and deviations from thermal equilibrium after reaching a target temperature. Since in our study, the sample did not have to be re-mounted between measurements and since we allowed for a 5 min equilibration time once the sample is in a \( \pm 1 \) K interval around each target temperature, the error was expected to be below \( \pm 2.5 \) K.

Resistance measurements were performed with triaxially shielded LF probes in two-point configuration. A four-point measurement was not necessary because of the high resistance of the sample. A Keithley 2612 A source measure unit was used in current sourcing mode (1.5 nA for measurements between 85 K and 280 K and 10 nA at 295 K) to measure the resistance. The measurement limit of this system is at about \( \sigma_{GeTe} = 2 \) nS cm\(^{-1}\) because at this resistance the maximal supply voltage of the SMU to drive the current is reached. Thus, measurements were performed only up to a lower limit of 115 K. The error in resistance is small compared to the error in temperature. All data shown are clusters of 20 measurements recorded over about 30 s at the end of the holding times at each temperature step.

For photo-conductivity measurements, the sample was illuminated with light from a Thorlabs LPS-830-FC pigtailed laserdiode. The energy of the light (830 nm = 1.49 eV) is higher than the bandgap of GeTe (ca. 0.75 eV), thus leading to photo-excited carriers. Steady-state illumination is controlled by an ITC4001 laser diode controller from Thorlabs calibrated to a photon flux of about \( 3 \times 10^{18} \) cm\(^{-2}\) s\(^{-1}\) at the sample position using a power meter. The light is fed into the cryostat with a HB800P fiber from Fibercore. All data shown are clusters of 20 measurements recorded over about 10 s at the end of an illumination time of 120 s. As the time to go to the next target temperature after illumination is about 15 min any photo-effect is assured to be decayed at the next dark-conductivity measurement.

3. Results

Conductivity and photo-conductivity measurements were performed between room temperature (RT) and 100 K to gain insight into the electrical transport behavior of the GeTe phase-change material. The dark-conductivity measured exhibits activated behavior (with an activation energy of 0.31 eV in the as-deposited amorphous state) between about 200 K and RT spanning more
than three orders in magnitude in conductivity (see figure 1). Below 200 K, the conductivity deviates from an activated behavior.

To evaluate the effect of drift, which is typically observed over time in phase-change materials, the sample was annealed at 370 K for 2 h to accelerate drift. After annealing, the temperature dependence of the conductivity below RT was measured again to monitor changes in the electrical transport behavior (blue curve in figure 1). This procedure was repeated for several, increasingly higher annealing temperatures and thus increasingly more drift. In each annealing step, the dark-conductivity decreases over the entire temperature range, whereas the temperature dependence is roughly preserved.

Steady-state photo-conductivity was measured after each dark-conductivity measurement to obtain an additional observable of the electrical transport in the GeTe phase-change material (see figure 2). This already allows a coarse interpretation on the basis of a very simple two-state model following Simmons and Taylor [18].

Their theory predicts three regimes of the photo-conductivity with decreasing temperature. At high temperatures down to a maximum, the photo-conductivity rises exponentially. After the maximum, the photo-conductivity falls exponentially till it becomes constant at very low temperatures.

In our data we observe a rise of the photo-conductivity up to a peak at around 250 K. Below 250 K, the photo-conductivity decreases steeply until about 180 K and shows a transition towards saturated behavior at even lower temperatures.

In the simple two-state model [18], which only allows a generic representation of traps above and below the Fermi level, the increase of photo-conductivity with decreasing temperature above 250 K is dominated by generation/recombination in a trap state between the Fermi level and the valence band. The energetic position of this state can be estimated by the slope of the photo-conductivity increase. In our case, the slope is roughly $E_{tr} = 0.07$ eV. With the Fermi level to be located at $E_F = 0.31$ eV above the valence band edge, as follows from the
slope of the dark conductivity (Figure 1), the energetic position of the trap state is $E_{t1} = E_F - E_{a1} = 0.24$ eV above the valence band edge.

According to the two-state model, the photo-conductivity in the temperature range below the peak temperature of $T = 250$ K is dominated by a trap between the Fermi level and the conduction band. Estimating its position from the slope of the photo-conductivity between 160 K and 200 K ($E_{t2} = 0.1$ eV) and assuming a bandgap of $E_g = 0.75$ eV [19], we get $E_{t2} = E_g - 2E_{a2} = 0.55$ eV above the valence band edge.

This very basic analysis already predicts a feature in the DoS at around $E_{t1} = 0.24$ eV, which indeed is also suggested by more sophisticated analysis of temperature- and frequency-dependent, modulated photo-conductivity experiments [19]. The second trap at $E_{t2} = 0.55$ eV can only be assumed to be sharp if a single activation energy is observed. As this is not the case in our data, the decay of the photo-conductivity to lower temperatures is only indicative of a broad unknown distribution of traps between the Fermi level and the conduction band edge. A more precise discussion is presented in the next section.

Upon annealing (drift acceleration), the photo-conductivity decreases over the full temperature range analogously to the dark-conductivity measurements. Again, the overall shape of the temperature dependence is not affected by the drift.

4. Discussion

The activated behavior of the dark-conductivity at temperatures above 200 K seems to be easily understandable in a simple trap-limited band-transport (TLB) picture with an activation energy of $E_a = 0.31$ eV in the as-deposited amorphous state. However, to understand also the deviation from the activated behavior at low temperatures and the decreased conductivity, it is helpful to explore a more precise DoS model. Longeaud et al proposed a model for the DoS of GeTe.
based on their measurements of the trap dynamics upon excitation with light [19]. This DoS consists of two parabolic bands extended by exponential tails and three Gaussian defect states as depicted in Figure 3(a). Assuming this DoS, we calculated the energetic distribution of electrons and holes by means of a simple charge-neutrality condition. From the number of free electrons and holes, the conductivity via transport in the valence and conduction band can be calculated assuming a band mobility of $\mu = -0.2 \text{ cm}^2 \text{Vs}^{-1}$ in both bands.

Localized carriers in the bandgap can also contribute to the transport via tunneling (hopping) directly from state to state. This contribution becomes increasingly important at lower temperatures where there is less energy available to excite carries into the bands. Following the approach by Longeaud and Tobbeche [20] and Marshall and Main [21], we calculated the contribution of variable range hopping (VRH) to the conductivity from the distribution of localized carriers in the gap. In Figure 4, the contributions from the three transport channels, free electrons and holes and localized carriers, are plotted. Above 170 K the simulated conductivity, which fits very well with the experimental data, is dominated only by holes. Even at the highest temperatures measured, the contribution from electrons is still more than one order of magnitude lower. Below 170 K, the conductivity is dominated by localized carriers. Hopping in the defect densities predicted by the simple two-state model and in more detail by Longeaud et al leads to a deviation from the activated behavior observed at high temperatures, which eventually results in a much lower activation energy of about 0.05 eV stemming from the energy difference between the defect densities and the Fermi level.

Upon annealing the dark-conductivity is reduced over the entire temperature range. For the sake of clarity, we will discuss only the highest annealing temperature. A previous study showed that the bandgap of GeTe widens upon annealing up to 100 meV depending on the annealing conditions [22]. For doped Sb–Te, it was shown that an opening of about 12% for similar annealing conditions as applied here is sufficient to explain the decrease of conductivity [23]. Hence, we simulated the conductivity for a DoS stretched by 12%, i.e. because all states moved relative to each other, the band edges as well as the defect states are 12% further away from the Fermi level.

![Figure 3.](image)

**Figure 3.** (a) DoS proposed by Longeaud et al [19], with parabolic bands, exponential tails, a Gaussian distributed donor density and two Gaussian acceptor distributions. (b) DoS stretched by 12% as proposed for a fit to our experimental data of dark- and photoconductivity of the annealed (drifted) sample (cf main text). Band edges and defect states are 12% further away from the Fermi level.
from the Fermi level than in the original DoS (cf figure 3(b)). This leads to an increase in the activation energy for both band transport at high temperatures as well as hopping at low temperatures. Thus, over the entire temperature range, the conductivity is decreased, which describes our experimental data well. It is important to note, that the relative shift of the defect levels is critical because they determine the position of the Fermi level. An increase of the bandgap alone with the defect levels staying at the same relative position to the valence band would have resulted only in a decrease of the irrelevant electron contribution to the transport. Interestingly, the decrease of the hopping conductivity can be explained solely by the shift of the defects due to the DoS stretching, i.e. the larger energetic hopping distance. A decrease in the defect density is not necessary to explain the data. As briefly discussed above, the basic shape of the temperature-dependent photo-conductivity can already be explained with a simple two-state model. A more precise analysis is possible by simulating the photo-conductivity with the same DoS as used above to describe the dark-conductivity data. The calculation was performed using a numerical simulator, DeOSSt, developed at the Laboratoire de Genie Electrique de Paris [24]. The capture coefficients describing the trap interactions were taken from Longeaud et al [19].

Simulation results are plotted in figure 5 together with the experimental data for the amorphous as-deposited phase and the highest annealing temperature. The simulation describes the as-deposited data fairly well, with all essential features being present. A perfect match to the data is not possible because hopping is not taken into account in the simulation software. The influence of the DoS stretching on the simulation is shown as dash-dotted orange line in figure 5. The experimentally observed shift of the peak photo-conductivity towards higher temperatures and the decrease of the photo-conductivity in the temperature range from 140 K to 240 K are captured by the model. However at low temperatures, the photo-conductivity approaches the same value as that of the unstretched case. In this regime, the carrier generation/recombination balance and thus the photo-conductivity becomes almost temperature-independent, and only the product of the trap density and capture coefficients determines the photo-conductivity. Thus,
only a change in one of those parameters can explain the experimentally observed decrease of the photo-conductivity below 125 K. For example, an increase in the defect density by a factor of 2 (dashed red line in figure 5) could account for the decrease in photo-conductivity at low temperatures.

5. Conclusion

In conclusion, transport in amorphous GeTe can be explained by TLB with an activation energy of 0.31 eV carried by holes above 170 K. Below this temperature, VRH via localized states about 0.05 eV from the Fermi energy dominates the dark-conductivity. Upon annealing, which accelerates the drift behavior that also occurs at RT, the conductivity decreases in both transport regimes. This can be explained using a DoS-based simulation solely by a stretching of the DoS by about 12%, which shifts defects and band edges away from the Fermi level. A change in the number of defects is not necessary to explain resistance drift because the increase of activation energy due to the DoS stretching is dominating. However, photo-conductivity measurements suggest that the DoS stretching might be accompanied by a slight increase of either the defect density or the capture coefficients. The same conclusion has been drawn to explain resistance drift in doped Sb–Te [23] a phase change material from the other side of the phase diagram of the Ge–Sb–Te ternary alloy system. For the most widely studied Ge$_2$Sb$_2$Te$_5$ a similar DoS [15] as for GeTe and band gap widening with time [25] has been reported. This suggests, that the findings are most likely applicable to phase change materials in general, even though this study focused on GeTe.

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