

Changes in Electrical Transport of Amorphous Phase Change Materials Upon Annealing

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ABSTRACT

While phase change memory technology has become more mature in recent years, fundamental problems linked to the electrical transport properties in the amorphous phase of phase change materials remain to be solved. The increase of resistance over time, called resistance drift, for example, prompts a major challenge for the implementation of multilevel storage which eventually is necessary to compete in terms of high storage densities.

A lot of studies have been performed to gain better understanding of resistance drift and the underlying transport mechanism. Thus, the literature on the phenomenological description of resistance drift and its time and temperature dependence[1] on one side and theoretical studies of the structure of amorphous phase change materials on the other side is broad. However, to link structural changes 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.

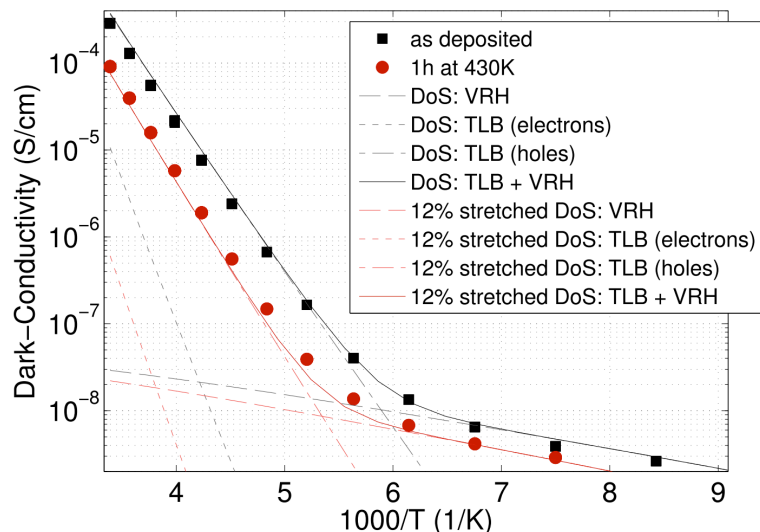


Figure 1: Dark-conductivity as a function of temperature before (black squares) and after annealing at 430 K (red circles). The black line is simulated using the DoS proposed in [5]. Stretching the DoS by 12% results in the simulated red full line. The hole (dash-dotted) and electron (dotted) contribution to trap limited band transport as well as the variable range hopping contribution (dashed) to the conductivity are also derived from the simulations.

In this work, we present temperature dependent conductivity and photo-conductivity measurements on GeTe and other phase change materials[2]. It is shown that trap limited band transport (TLB) at high temperatures (above 165 K for GeTe) and variable range hopping (VRH) at low temperatures is the dominating transport mechanism (see Figure 1). After annealing for 1 h at 430 K to accelerate drift in the material, the conductivity is decreased in both the TLB as well as the VRH regime.

Both transport mechanisms can be modeled when the density of states of the material is known. Given a DoS as input, the electron occupation statistics are obtained by calculating the position of the Fermi level as a function of temperature from charge neutrality condition. Once the occupation statistics is known trap limited band transport is calculated from the free charge carriers using a constant mobility. Variable range hopping within localized states in the gap is calculated from the occupation statistics using a mobility term that depends on the hopping probability between states following [6].

Based on measurements of the temperature dependence of the optical band gap[3], modulated photo-conductivity[4] and photo-thermal deflection spectroscopy[1] a DoS for GeTe has been proposed previously[5] (see Figure 2).

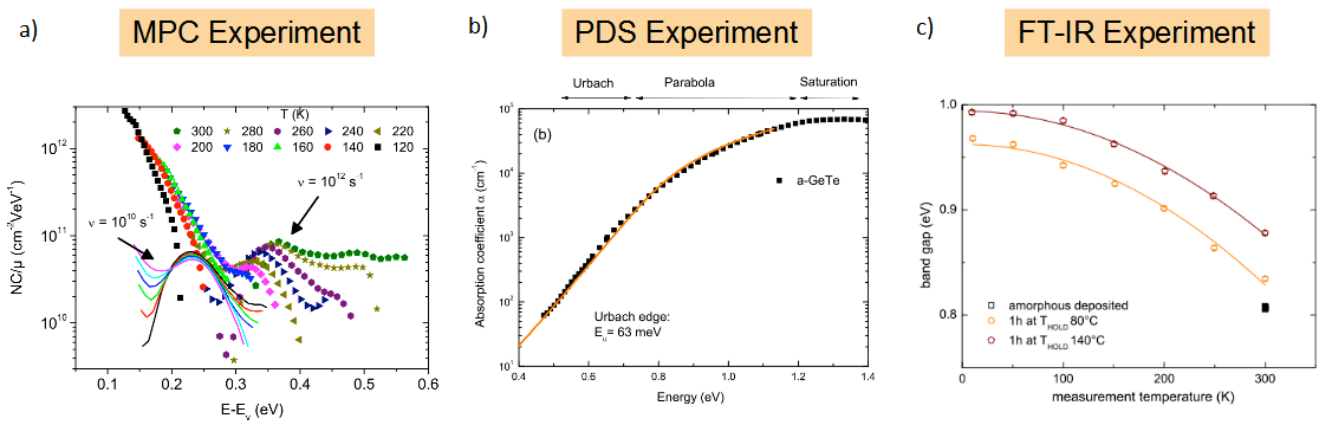


Figure 2: Measurements of the reduced density of states via modulated photocurrent a), absorption via photothermal deflection spectroscopy b) and temperature dependence of the optical bandgap via infrared spectroscopy c). From MPC a valence band tail of $\gamma = 31.8 \text{ meV}$ and a defect around 0.25 eV is identified. From PDS a conduction band tail width of $\gamma = 58.5 \text{ meV}$ can be derived. With FT-IR the temperature dependence of the bandgap can be quantified to follow $E_g(T) = E_0 - \zeta T^2$ with $E_0 = 0.825 \text{ eV}$ and $\zeta = 1.325 \mu\text{eV}/\text{K}^2$. [5]

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[2]. The decrease in conductivity upon annealing can entirely be explained by an increase of the band gap by about 12%. In the TLB regime the increase of the bandgap leads to an increased activation energy causing the reduced conductivity while in the VRH regime the increased bandgap and with it the increased energetic distance between defect states leads to a reduced hopping mobility.

While the above mentioned measurements on GeTe have been performed on the amorphous as-deposited phase, further studies have been performed on the melt-quenched amorphous phase in cells using a very different phase change material, doped Sb-Te[2] (see Figure 3). After a cell is RESET at room temperature it is heated up to an annealing temperature to accelerate drift. On the ramp down, the temperature dependence of the resistance is measured. This experiment is repeated, annealing to sequentially higher annealing temperatures.

Fitting $R = R_0 \exp(E_a/(kT))$ to the experimental data around room temperature we observe an increase of the activation energy E_a of about 15 meV and an increase of the pre-exponential factor R_0 by 2.5 for the highest annealing temperature (Figure 3c).

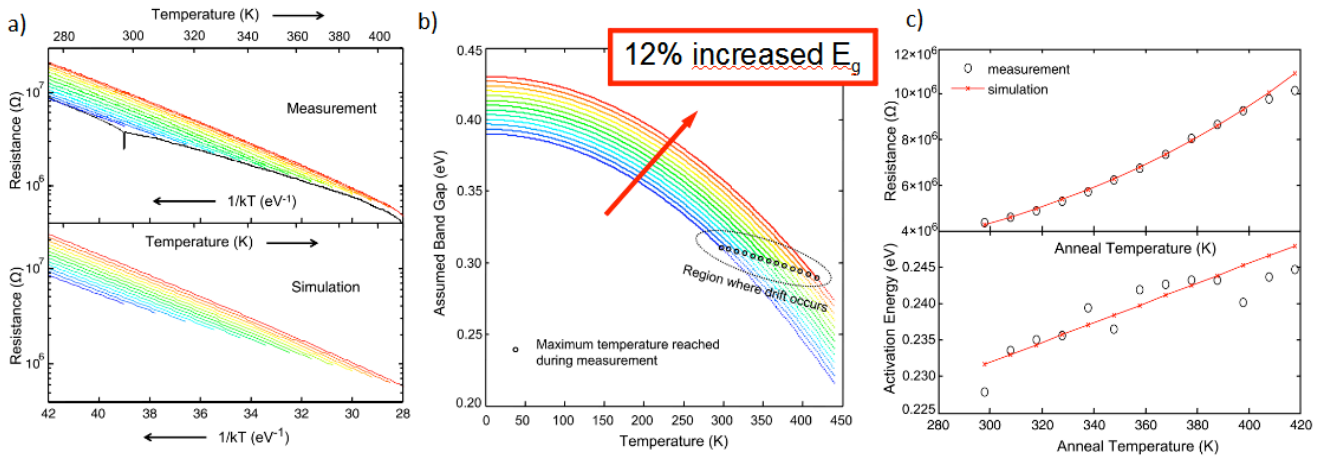


Figure 3: Simulated and measured temperature dependence of the cell resistance as a function of drift (blue to red) a). While the resistance at room temperature increases by a factor of 2.5 for the highest annealing step the measured activation energy increases upon drift by about 15 meV c). This behavior can be well described by a temperature dependent bandgap of $E_g(T) = E_0 - \zeta T^2$ with $E_0 = 0.39$ eV and $\zeta = 0.9 \mu\text{eV}/\text{K}^2$ and a bandgap increase upon annealing by 12%. The rather small change in activation energy but large change in pre-exponential factor is due to the almost linear temperature dependence of the bandgap around room temperature.[2]

This increase can be explained assuming a bandgap with similar temperature dependence as GeTe, which increases by 12% at the highest annealing step (Figure 3b). Assuming a fixed relation between bandgap E_g and activation energy $E_a = E_g/2$ Even though only the activation energy is changing upon drift, part of this change will contribute to a change in the pre-exponential factor. Because the bandgap is varying almost linear around room temperature resulting in $E_a = E_0^* - c T$, the resistance can be written as $R = R_0 \exp(-c/k) \exp(E_0^*/(kT))$. Therefore, the change in E_0^* upon drift reflects the change in the measured activation energy and the change in the linear component c causes a change in the pre-exponential factor.

Based only on the assumption that the same mechanism observed in GeTe is responsible also for the increase in resistance in doped Sb-Te, a good match between experimental results and simulation is achieved (Figure 3a and 3c). These results show that drift in very different phase change materials can be attributed to a similar large increase of the bandgap upon annealing indicating that the observed reason for drift might be universal for phase change materials.

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