

Controlling Charge Transport in Crystalline Phase Change Materials

M. Wuttig¹, T. Siegrist^{1,2}, M. Woda¹, S. Kremers¹, P. Merkelbach¹, and P. Jost¹

¹ I. Physikalisches Institut, RWTH Aachen University, 52056 Aachen, Germany

² Department of Chemical and Biomedical Engineering, Florida State University, Tallahassee, FL 32312
wuttig@physik.rwth-aachen.de

ABSTRACT

Phase change materials are one of the most promising materials for emerging electronic data storage applications. By application of a short voltage pulse they can be rapidly and reversibly switched between the crystalline and amorphous state. The pronounced change of resistance upon crystallization, which often spans more than four orders of magnitude, is particularly attractive, since it should enable multilevel storage. This storage attribute is crucial to compete with ongoing developments in flash memories. In addition, it was recently shown that devices could be reversibly switched in 4 nanoseconds reaching DRAM like speeds. The combination of high switching speeds and non-volatility might even help to establish this memory as a universal memory replacing both Flash and DRAM. This appears feasible if the power consumption upon reading, writing and erasing bits can be minimized. The most power-demanding step is the erasure of a bit that is achieved by local amorphization of a previously crystalline region. The necessary power could be significantly reduced if phase change materials with a higher resistance in the crystalline phase would be available. In this case, heating efficiency is enhanced. Therefore we have focused on a systematic understanding of the charge transport in amorphous and crystalline phase change materials. The goal of these studies is the identification of the dominant scattering mechanism as well as the development of concepts to modify this scattering mechanism. It will be shown, that certain crystalline phase change materials utilize a highly unusual charge transport mechanism, which employs Anderson localization. This finding is in striking contrast to the behaviour of ordinary semiconductors and proves that crystalline phase change materials form an extraordinary quantum state of matter. The relevance of these finding for our understanding of crystalline solid will be discussed as well as the consequences for data storage applications.

Key words: crystalline phase change materials, charge transport, effect of annealing

1. INTRODUCTION

Few properties have provided such a wealth of information on solids as measurements of charge carrier transport. The electrical resistivity in particular is highly valuable to characterize solids, since it varies by more than 32 orders of magnitude. Two different types of solids can be distinguished based upon the temperature dependence of their resistivity, or the reciprocal quantity, the electrical conductivity. While the conductivity of insulators vanishes as T goes to 0 K, metals reveal a finite conductivity. This immediately raises the question if there is a minimum conductivity for metals. Indeed, Mott argued that no metallic state at 0 K should be possible below a minimum conductivity. Experimental investigations of doped semiconductors, however, show a conductivity in the metallic state that is lower by at least three orders of magnitude, in line with scaling theory. This finding immediately raises questions on the nature of the transition from the metallic to the insulating state. Several concepts to explain a metal-insulator transition (MIT) have been established. According to Mott, a metal-insulator transition can be achieved if the electron correlation exceeds a critical value. A second route to insulating behavior has been identified by Anderson, who showed that increasing disorder turns a metal with delocalized electronic states at the Fermi energy into an insulator with localized states. Experimentally it is very difficult, though, to separate aspects of disorder and electron correlation, hence the transition observed in doped semiconductors is usually discussed as a combined Mott – Anderson transition. To our knowledge no three dimensional crystalline solid is known, where the MIT can solely be accounted to a varying degree of disorder (Anderson localization).

2. EXPERIMENTS

To unravel the transport mechanism of the charge carriers we have performed an in-depth characterization of transport properties. Figure 1. top shows as an example the resistivity upon heating and subsequent cooling down to room temperature of an amorphous film of GeTe (thickness: 80 nm) deposited onto a glass substrate. Initially the amorphous film has a high sheet resistance of $268 \text{ M}\Omega$, which decreases upon heating. At approximately 465 K a sudden drop in resistance is observed which is followed by a structural rearrangement into the rhombohedral α -phase of GeTe. Upon cooling down from 595 K to 300 K the sample shows an almost temperature independent sheet resistance of $75 \text{ }\Omega$. Hence the resistance of the GeTe film has decreased by more than six orders of magnitude upon crystallization. This large change is very attractive since it opens the possibility to produce potentially a large number of in between resistance values if amorphous or crystalline regions of different size could be produced in a controlled manner in a phase change (PC) memory cell.

To study this possibility in more detail, a larger number of phase change materials with different stoichiometry were investigated to determine the resistance change upon crystallization and identify the best possible material for multilevel storage. Interestingly enough, the different materials could be classified into two different groups regarding the change of resistance in the crystalline state upon increasing annealing temperature. While all materials showed an abrupt change of resistance upon crystallization, the resistance in the metastable crystalline phase showed different temperature dependencies. A material which showed a behavior different from GeTe is depicted in fig. 1. bottom, where the sheet resistance of a thin film of $\text{Ge}_1\text{Sb}_2\text{Te}_4$ is displayed upon heating and subsequent cooling. Initially the film is in the as-deposited amorphous state. Upon heating to 425 K with a heating rate of 5 K/min, the film crystallizes. This is accompanied by a drastic decrease in resistance. Immediate cooling to 300 K gives a resistance value of $5 \times 10^4 \text{ Ohm}$. Upon subsequent heating to 450 K and cooling back down to room temperature, a considerably lower value of 10^4 Ohm is observed. The annealing temperature was increased in steps up to 535 K, which led to a further reduction in resistance of the crystalline state at room temperature to $3 \times 10^2 \text{ Ohm}$. Hence upon annealing, the resistance of the crystalline phase has decreased by more than two orders of magnitude. Equally remarkable is the change in the slope of the sheet resistance as a function of temperature. Both observations are indicative of a significant change of electronic transport in the crystalline state with increasing **annealing** temperature. A similar decrease of the electrical resistance upon increasing annealing temperature is also observed for $\text{Ge}_2\text{Sb}_2\text{Te}_5$. This change in resistance has been attributed to different mechanisms including the presence of trapping sites at grain boundaries together with a variable electron concentration, similar to the scattering mechanism observed in polycrystalline silicon with different doping levels. In this model, the trapping of charge at the grain boundaries produces potential barriers that are screened with increasing electron concentration (with increasing anneal temperature), thus lowering the resistance of the material. It is important to note, that the mechanism proposed so far should be active in all phase change materials. Interestingly enough, we observe instead that only a subgroup of phase change materials shows this behavior, while other materials such as GeTe do not display a pronounced change of resistance with increasing annealing temperature after the initial crystallization.

3. RESULTS & DISCUSSION

In this study we will demonstrate the mechanism responsible for the transition between the insulating and metallic state of the crystalline phase change film observed in $\text{Ge}_1\text{Sb}_2\text{Te}_4$ is disorder induced localization. A variety of experiments were performed and analyzed to derive this conclusion as will be described in detail.

4. CONCLUSION

The transition from insulating to metallic charge transport behavior observed in step-annealed films of $\text{Ge}_1\text{Sb}_2\text{Te}_4$, $\text{Ge}_1\text{Sb}_4\text{Te}_7$, $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and $\text{Ge}_3\text{Sb}_2\text{Te}_6$ can be understood as a disorder induced MIT, driven by a change in charge carrier mobility (or scattering rate) at almost constant charge carrier density. This is in contrast to systems where the charge carrier concentration is varied to achieve the MIT, as for instance in Si:P with various phosphorus doping levels.

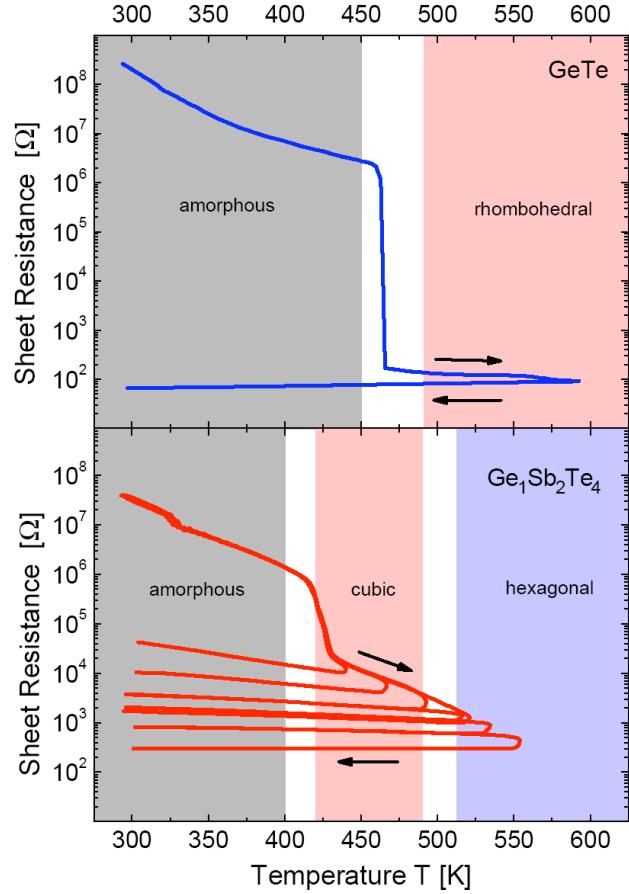


Figure 1.: Temperature dependent resistance of a 80 nm thick GeTe film (top) and $\text{Ge}_1\text{Sb}_2\text{Te}_4$ (bottom) on a glass substrate measured in the van-der-Pauw geometry (Ref.) The as-deposited amorphous film has a sheet resistance of $268 \text{ M}\Omega$ for GeTe and $40 \text{ M}\Omega$ for $\text{Ge}_1\text{Sb}_2\text{Te}_4$. Upon heating in Argon atmosphere with 5 K/min the sheet resistance decreases and drops rapidly due to the crystallization of the films. For $\text{Ge}_1\text{Sb}_2\text{Te}_4$, it can be seen that the room temperature resistance of the crystalline phase decreases by a factor of approximately 200 upon increasing the annealing temperature from 425 K to 535 K . Equally noteworthy is the change in the slope of the curves with increasing annealing temperature.

Biography

Since 1997 Full Professor of Physics at the University of Technology, Aachen, Germany; Head of Research Group: Physics of novel Materials, Research mission: prepare and characterize novel materials with unique optical and electronic properties. Conduct research in the fields of: a) chalcogenide based semiconductors, b) organic materials for opto-electronic applications, c) optical functional coatings.

Speaker of the Strategy Board of RWTH Aachen (since 2009), Dean of the Faculty of Science, Mathematics and Computer Sciences (2006-2008)Visiting professor at CRMC² - CNRS Marseille (4/1995), AT&T Bell Laboratories, Murray Hill (1995-1997), Hangzhou University (8/1998), Kenyatta University (1999), IBM Research Center Almaden (Spring 2006), Data Storage Institute Singapore (10/2007), Shanghai Institute of Microsystems and Information, Chinese Academy of Sciences (8/2009), Stanford University (Spring 2010), Lawrence Berkeley National Laboratory (Summer 2010)

Several national and international awards