Recent Progress in Understanding PC-Materials for Optical and Electronic Storage

Christoph Steimer , Wojciech Welnic , Ralf Detemple, Daniel Wamwangi, Henning Dieker and Matthias Wuttig
I. Institute of Physics (IA), RWTH-Aachen University, Sommerfeldstr. 14-18, 52056 Aachen, Germany

ABSTRACT

At present, phase change media that can meet the increasing demands of modern storage technology are developed in industrial and university labs employing experimental optimisation schemes an. Merely by try and error, for a large number of samples it could be shown that only materials with cubic or near-cubic structures show the required optical contrast for phase change recording as opposed to materials based upon tetrahedral coordination. Here we present an alternate approach, which is based upon both combinatorial techniques to produce sample libraries and ab initio calculations of the ground state and electronic structure. The calculations explain the variation of the ground state structure and the bonding type with stochiometry Understanding the observed trends and combining them with an understanding of the kinetics of the phase transitions promises the directed optimisation of future phase change media.

Key words: phase change storage, density functional theory, stoichiometry, crystalline and amorphous structure

1. INTRODUCTION

Phase change (PC) materials have been in commercial use in rewritable optical storage (DVD-RW e.g.) for a decade and are currently investigated as nonvolatile electronic storage to replace conventional FLASH-memory: A ps-duration laser or current pulse of high intensity is used to melt a sub-micron sized spot of crystalline material and quench it to the amorphous state. A second pulse of lower intensity but longer duration leads to a less pronounced spatial temperature profile and lower cooling rates but provides suffcient thermal energy to activate the crystallisation process. Since reflectivity and conductivity of the amorphous state are lower than the crystalline values, a third laser - or current pulse, even lower in intensity and thus not changing the material, can be used to read out the current state of the bit [13]. Surprisingly, despite their commercial application material development of PC-media still heavily relies on empirical approaches. This contribution summarizes how stoichiometry determines the structure of the crystalline and the amorphous phase.

2. STOICHIOMETRY & STRUCTURE

Based on their different compositions and their different crystallisation behaviour common PC-materials can be devided into a Sb-rich and Te-rich class, which are based on Sb_2Te or Sb_2Te_3 and are growth -or nucleation dominated [12,13]. Two of the phases formed upon annealing of AgIn doped Sb_2Te are $AgInTe_2$ and $AgSbTe_2$, which were chosen as model-systems [4]. After molecular beam deposition on glass-substrates, the samples were crystallised by annealing in a N_2 -atmosphere. A static tester was used to laser amorphise a spot of a diameter of about 0.3 µm to start out from identical conditions. The reflectivity of the amorphous spot was measured before exposure to a crystallisation pulse of defined intensity and duration and a second measurement of the reflectivity with the same laser. The procedure was repeated for an array of spots with varying intensities and durations of the crystallisation pulse. The results are visualized in figure 2: While $AgSbTe_2$ shows an increase in reflectivity due to crystallisation expected for low intensities and long pulse durations, the low intensity wings for low power or short duration are followed by immediate ablation in the case of $AgInTe_2$. To understand the non-observable change in reflectivity, the sheet-resistance of as deposited samples was monitored upon annealing in a N_2 –atmosphere.
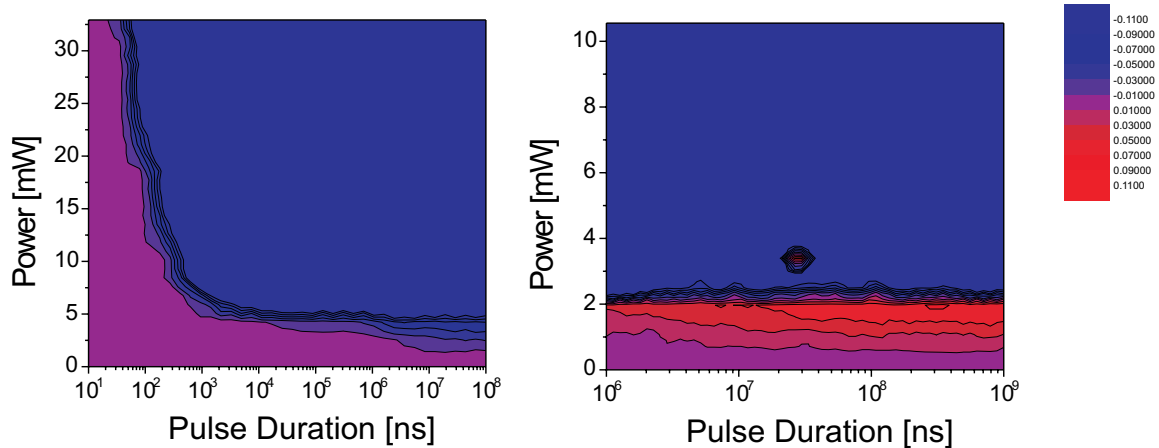
Fig. 1. Power-Time-Effect diagrams for AgInTe$_2$ (left) and AgSbTe$_2$ (right). Both, reflectivity measurements and crystallisation pulses were performed with the same laser-diode and optics at 780 nm. The greyscale coded in-or decreases in reflectivity are attributed to crystallisation or ablation respectively [10].

Figure 2 shows the drop beyond 100$^{\text{o}}$ C together with the optical contrast, calculated from the optical constants determined before and after annealing. To relate the different contrasts to structure, XRD measurements were taken at the annealed samples and confirmed crystallisation in a chalcopyrite-structure, which is similar to a Zinc-blende structure, for AgInTe$_2$ and a rock salt-like structure for AgSbTe$_2$, where the Te-atoms occupy one of the sub-lattices while the remaining places are taken by Ag and Sb at random.
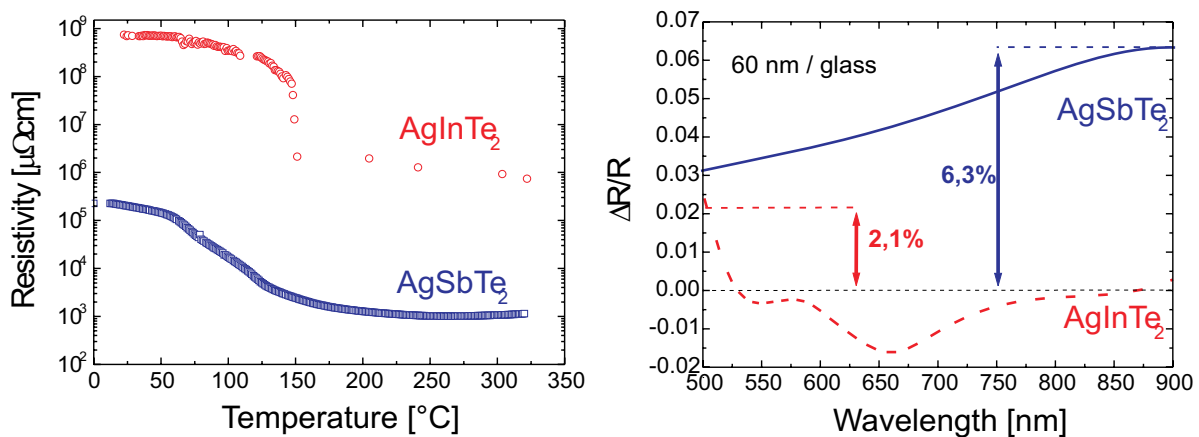

Fig. 2. Left: Sheet resistance of a 60 nm film on glass measured on annealing. Right: Optical contrast between amorphous and crystalline phase, calculated from ellipsometric measurements [4].

The formation of a chalcopyrite structure for chalcogenides with an average valence electron number up to four and of rock salt structures beyond that value can be understood by the electron density plot in figure 4, obtained from density functional theory [5]. Up to four valence electrons can be hosted in bonding sp^3 -orbitals leading to tetrahedral coordination. Beyond that value occupation of orthogonal p-orbitals is preferred to avoid the anti bonding sp^3 states and thus octahedral coordinations are assumed as found in simple cubic or rock salt arrangements for instance. The energy difference between a rock salt -and a chalcopyrite structure for various chalcogenide alloys as a function of the valence electron numbers obtained from DFT in figure 6 shows that this structural transition is a general rule for chalcogenides rather than a peculiarity of these very alloys [5]. This trend is reconfirmed by a compilation of experimental structural data, which also shows an insuffcient electrical and optical contrast for all tetrahedral

arrangements as opposed to the octahedral coordinations given in table 1. Despite of the same high relative Te-content the model-systems AgInTe$_2$ and AgSbTe$_2$ demonstrate, that not all chalcogenides are suitable phase change materials. The lower optical contrast on amorphisation of chalcopyrite-alloys as compared to the octahedral arrangements had been attributed to the lower density contrast between the crystalline and amorphous phase for quite a while.
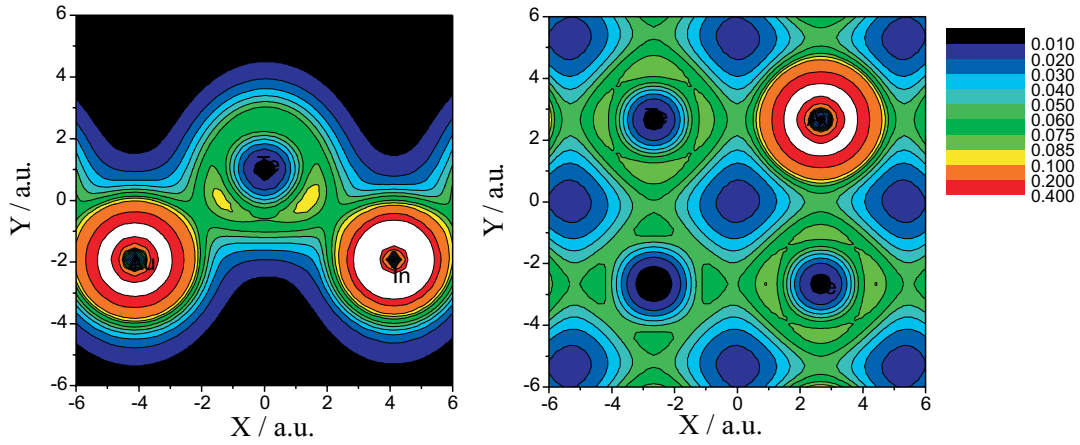

Fig. 3. Calculated electron-densities in arbitrary units for the (100)-and (111)plane of AuInTe2 (left) and AuSbTe2 (right) with average valence electron numbers of 4.0 and 4.5 [5].

electrical and optical contrast for all tetrahedral arrangements as opposed to the octahedral coordinations given in table 1. Despite of the same high relative Te-content the model-systems AgInTe$_2$ and AgSbTe$_2$ demonstrate, that not all chalcogenides are suitable phase change materials. The lower optical contrast on amorphisation of chalcopyrite-alloys as compared to the octahedral arrangements had been attributed to the lower density contrast between the crystalline and amorphous phase for quite a while. To overcome this over-simplified picture and understand the property contrast in more detail, we will present a model for the amorphous short range order of PC-materials with compositions along the GeTe-Sb$_2$Te$_3$ pseudo-binary line in the next chapter.
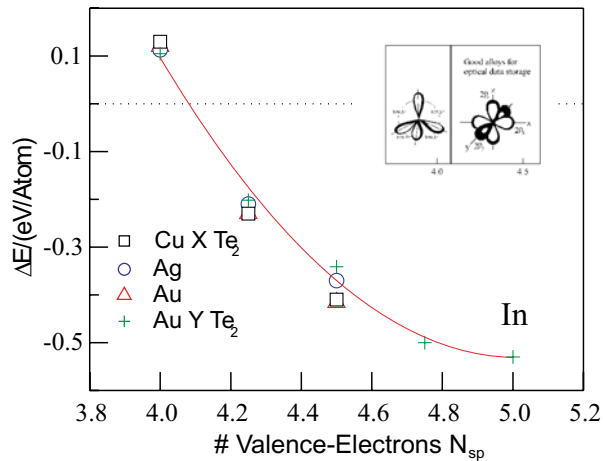

Fig. 4. Energy difference between rock salt -and chalcopyrite structure, calculated by DFT for different model-alloys with varying number of valence electrons. X = Cd, In, Sn, Sb; Y = Ga, Ge, As, Sb; see [5] for details.

	Material	Structure	Nsp
Unsuccessful samples	AgInTe2	Chalcopyrite	4.00
	AuInTe2	Chalcopyrite	4.00
	In3 SbTe2	Rock Salt	4.30
Successful samples	Au25 Ge4 Sn11 Te60	Cubic	4.45
	AgSbTe2 AuSbTe2	Rock Salt Cubic	4.50 4.50
	GeSb2 Te4 GeSb2 Te4 Ag3 In4 Sbn76 Te17 GeTe Ge4 Sb1 Te5	Rock Salt (metastable) 4.75 Hexagonal (stable) Rock Salt (metastable) 4.80 Cubic Rock Salt (metastable) 5.00 Rock Salt (metastable) 5.10	5.43 4.93

Table 1. Crystalline structures and average valence-electron numbers for some chalcogenides, showing sufficient or insufficient contrast for optical storage, depending on their crystalline structures or average valence electron numbers Nsp espectivrely respectively[5]. For alloys like $Ge_1Sb_2Te_4$ with a rock salt-like metastable structure, where one sub-lattice is occupied by Te and the other one shared by 2 Sb, 1 Ge and 1 vacancy, the vacancies were counted in the denominator as atoms to determine average electron numbers N_{sp}. Note that a) not all Te-rich chalcogenides are suitable and b) not all successful materials contain Ge.

3 AMORPHOUS SHORT-RANGE ORDER AND CONTRAST

Figure 5 reflects the optical properties of amorphous and crystalline GaAs and $Ge_2Sb_2Te_5$ by the relative dielectric constants and absorption. The amorphous phase of GaAs follows the dielectric functions of the crystalline phase except for a damping of the sharper features that are smeared-out to some extent by deviations from perfect order. Nevertheless the relative variation is on the order of 25%. The situation is totally different for the phase change alloy $Ge_2 Sb2 Te5$ where differences as large as 150% appear.
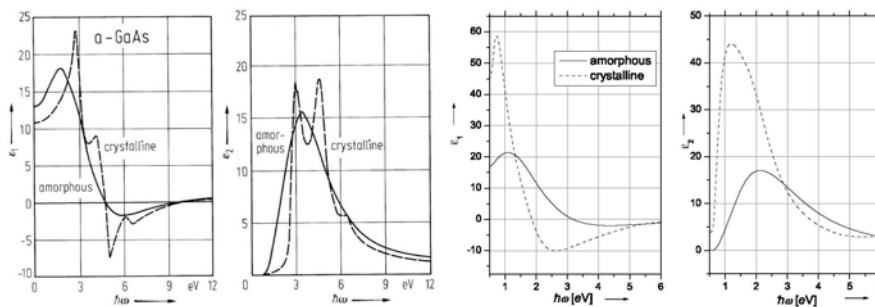

Fig. 5. Real and imaginary part of the dielectric functions over energy for GaAs from Landolt Börnstein and $Ge_2Sb_2Te_5$ (right) in the crystalline and amorphous phase respectively. To compare the difference for both states note the different scales.

Such an extraordinary difference in the electronic and optical properties and the rapid crystallisation of PC-alloys can only be explained in terms of large structural changes appearing on short length-scales as these length-scales govern the electronic structure and can be quickly rearranged. Figure 6 gives the Fourier-transformed EXAFS-Signal for GaAs and $Ge_2Sb_2Te_5$ in the amorphous and crystalline phase. The signal measured at the k-resonance of Ga, As, Ge or Te gives the pair-correlation and thus the short-range order in the vicinity of the respective atoms. The difference in

the short-range order between the amorphous and crystalline phase is much lower for the GaAs-data taken from literature than for the recent measurements of Kolobov et al. on $Ge_2Sb_2Te_5$ [6].
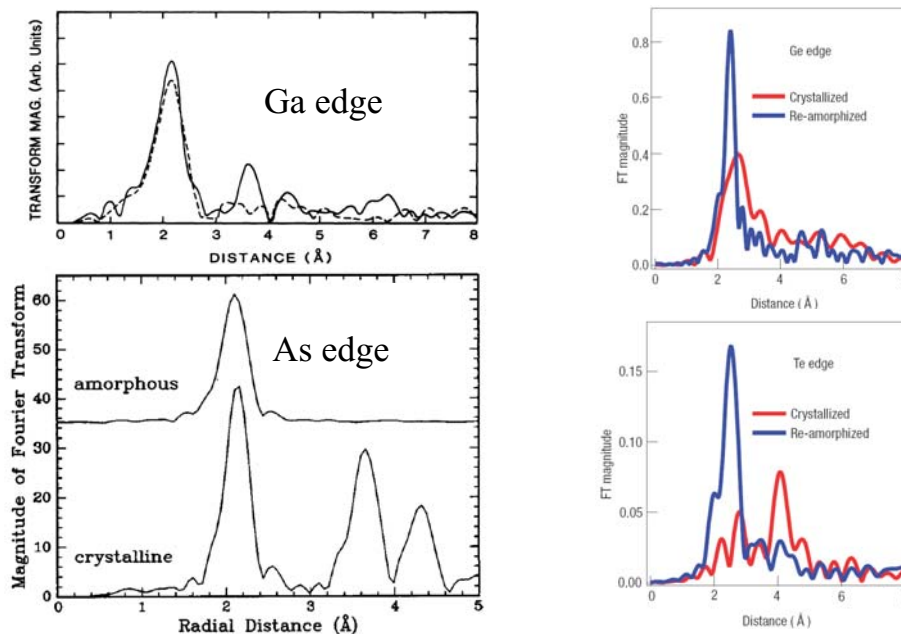

Fig. 6. Compilations of Fourier-transformed EXAFS-signals for the Ga-and As-edge of GaAs (left) [7,8] and the Ge- and Te-edge of $Ge_2Sb_2Te_5$ (right) [6] in the crystalline and amorphous phase from Rigday, Bouldin, Kolobov and their respective coworkers.

Kolobov suggested, that Ge switches from an octahedral to a tetrahedral coordination on amorphisation. Based on that model, we chose $Ge_1Sb_2Te_4$ because of it's smaller unit-cell, that was modeled by an array of 4^3 sites, as shown in figure 8.
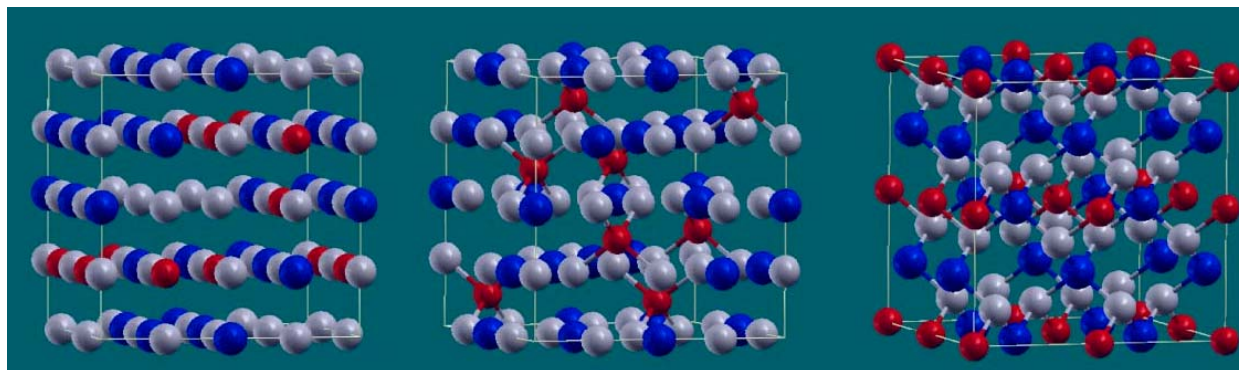

Fig. 7. Structures obtained after Molecular Dynamics relaxation of the ideal rock salt -, spinel -and chalcopyrite structures used a an input for the DFT-calculations of the ground-state energy [9].

We started out from a conventional rock salt structure, where 4 Te-atoms occupy the A-sites while 1 Ge-, 2 Sb-atoms and 1 vacancy share the B-sites, to model the crystalline -and a spinel structure to represent the short range ordering of the amorphous phase. The spinel structure can be thought of as a mixture of the rock salt -and the chalcopyrite structure, as it offers tetrahedral arrangements for the Ge atoms but maintains octahedral coordinations for Sb and Te. We varied the lattice constants and allowed the atoms to relax from their ideal initial positions [9].
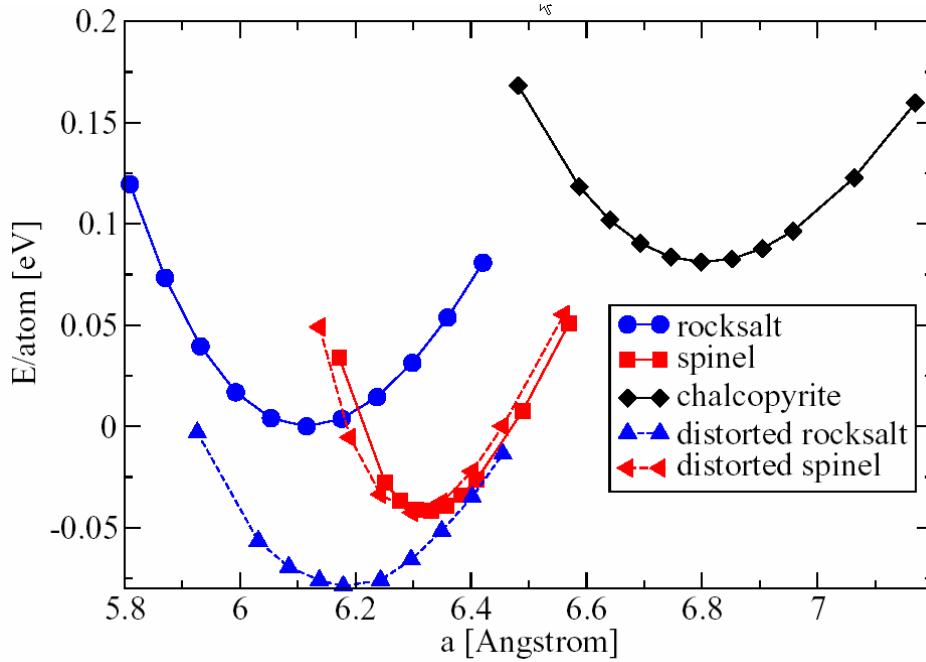
Fig. 8. Ground-state energy vs. lattice constant for the ideal and relaxed rock salt -, spinel -and chalcopyrite structure as given in figure 7. Due to its negligible energetic and structural relaxation the ideal chalcopyrite-values are shown only.

Figure 8 shows, that the lowest energy is reached for a slightly relaxed rock salt structure at lattice constant of about 6.2 Å while the relaxed spinel structure has a energy minimum at about 6.3 Å that is 40 meV/atom higher only in energy. This shift to higher lattice constants and energies in the spinel-like arrangement is well in line with the comparatively large density loss of the cubic crystalline structures of phase change alloys of about 5% as compared to 2% observed for the chalcopyrite alloys and recent differential scanning calorimetry-results [11]. Overmore that density change combined with the pronounced change from octahedral to tetrahedral coordination of the Ge-atom on amorphisation explains not just why the phase change alloys with cubic crystalline structures show such an pronounced change in optical properties but also why phase change alloys with crystalline chalcopyrite structure and thus tetrahedral arrangements in both phases lack that contrast. However it should be noted, that the most pronounced differences in the electronic structure of both phases are related to the Te-and Sb-bands rather than Ge. Figure 9 shows the difference of the density of states between the relaxed rock salt -and spinel structures for all atoms and for the s- and p-bands for each element. The difference of the overall density of states shows an increased density of states just below the Fermilevel (0 down to −5 eV), which fits to the semiconductor-metal-transition and the optical contrast in the visible range observed on crystallisation. This difference can be attributed mostly to the p-orbitals of Te, as Ge- shows a broad change in the s-band well below the energies relevant to optical properties only but almost no difference in the p-band at all. The situation is similar for the narrow changes in the Sb s-and p-band. Their influence is further decreased by their lower concentration in the alloy as compared to Te. The pronounced increase in the Te-p- band is easily identified in the overall difference of the density of states and is responsible for the electronic and optical changes upon crystallisation/amorphisation. While a confirmation of our DFT-results by EXAFS- measurements on this alloy is still due, we believe, the outcome agrees well with Kolobovs results [6] and explains the large density and optical/electronic contrast.
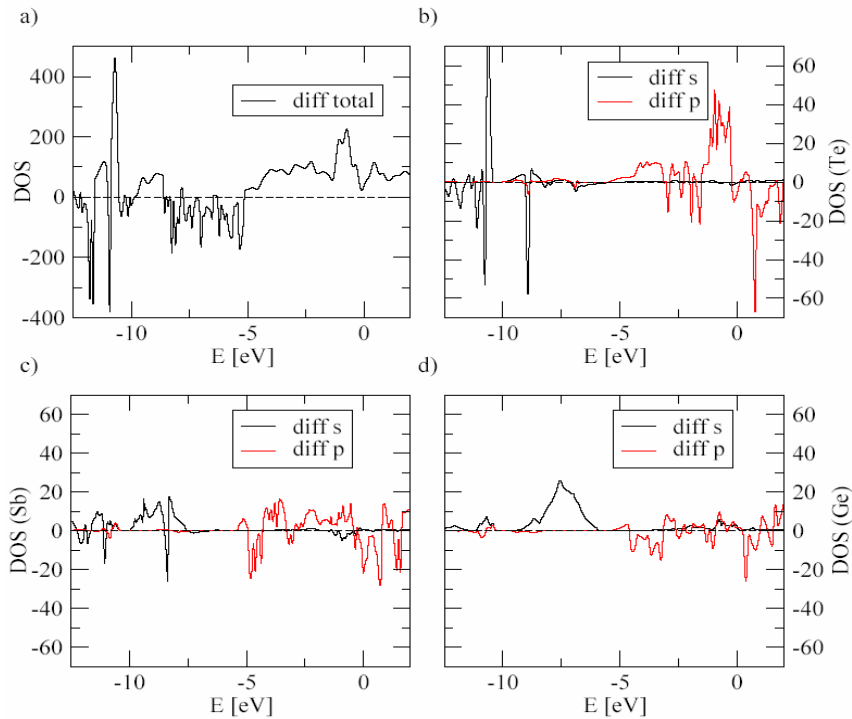
Fig. 9. Difference in the density of states between a rock salt and a spinel like arrangement for all elements and band (a) and s- and p-bands of the single elements (c-d).

4. CONCLUSION

Crystalline chalcogenide alloys for PC-storage either assume chalcopyrite structures with a low -or cubic structures with a high optical contrast to their amorphous phase. Both crystalline structures can be understood in terms of their coordination numbers and predicted from stoichiometry by their average number of valence electrons. For the alloys that crystallise in octahedral coordination we suggest a spinel-like short range order for the amorphous phase with the Ge-atoms in fourfold coordination, that does not involve longrange diffusion on switching. That change in the Ge coordination on crystallisation to the cubic phases explains both the pronounced difference in the opto-electronic properties as well as its absence for the crystalline chalcopyrite structures, where coordination is likely to be maintained on amorphisation. This interpretation is further backed up by the lattice expansion of the spinel phase, that could account for the higher density loss of the crystalline cubic phases of about 5% as compared to about 2% for the chalcopyrite phases on amorphisation. Future work should focus on kinetics to establish a similar understanding of the influence of stoichiometry on that field. From the structural point of view, other classes of phase change materials without Ge e.g. are the next promising field to be investigated in their amorphous phase, as they are supposed to show a different switching mechanism.

REFERENCES

1.   S. Ovshinsky: Phys. Rev. Lett. 21, 1453 (1968)
2.   V. Weidenhof, I. Friedrich, S. Ziegler, M. Wuttig: J. Appl. Phys. **89**, 3168 (2001)
3.   M. Wuttig, R. Detemple, I. Friedrich, W. Njoroge, I. Thomas, V. Weidenhof, H. Woeltgens, S. Ziegler: J. Magn. Magn. Mat. **249**, 492 (2002)
4.   R. Detemple, D. Wamwangi, M. Wuttig, G. Bihlmayer: Appl. Phys. Lett. **83**, 2572 (2003)

5.   M. Luo, M. Wuttig: Adv. Mat. 16, 439 (2004)
6.   A.Kolobov, P.Fons, A.Frenkel, A.Ankudinov, J.Tominaga, T.Uruga: Nat. Mat. 03, 703 (2004)
7.   M. Rigday, C. Glover, G. Foran, M. Yu: J. Appl. Phys. 83, 4613 (1998)
8.   C. Bouldin, R. Forman, M. Bell et al.: Phys. Rev. B 35, 1429 (1987)
9.   W. Welnic, R. Detemple, C. Steimer, M. Wuttig: Nat. Mat. 05, 56 (2006)
10.   R. Detemple: Dissertation RWTH-Aachen Germany (2003)
11.   M. Klein, RWTH-Aachen Germany, private communication (2006)
12.   J. Kalb et al.: Appl. Phys. Lett. 84, 5240 (2004)
13.   J. Kalb et al.: Journ.Appl. Phys. 98, 054910 (2005)

Biography

Christoph Steimer, born in 1970, studied physics at the University of Saarbruecken and finished his Diploma on Xray Diffraction on solid surfaces in 1997 . He moved to the FZ-Juelich to investigate surfaces by Scanning Tunneling Microscopy and surface sensitive spectroscopies to obtain his PhD in physics from the RWTH-Aachen in 2001. He worked on SiGe-transistors for Infineon-Technologies in Munich before he went to Harvard later that year to work on liquid surfaces by Xray-Diffraction and Reflectivity. In 2003 he returned to Germany to take responsibilities in the phase-change group of Matthias Wuttig at the RWTH-Aachen. The main focus of his work are material-science with particular emphasis structural aspects of surfaces and interfaces and the development of phase-change materials.