

Phase-Change Materials: The Importance of Resonance Bonding

Dominic Lencer¹, Kostiantyn Shportko¹, Stephan Kremers¹, Michael Woda¹, John Robertson² and Matthias Wuttig³

¹Institute of Physics (IA), RWTH Aachen University, 52056 Aachen, Germany

²Engineering Department, Cambridge University, Cambridge CB2 1PZ, UK

³JARA-FIT, RWTH Aachen University, 52056 Aachen, Germany

ABSTRACT

Among the various demands materials have to meet in order to enable phase-change applications, the most obvious one is sufficient property contrast between the amorphous and crystalline state. This contrast is attributed to a pronounced change in bonding between the two phases. While the amorphous phase exhibits coordination and properties expected for ‘ordinary’ covalent systems, we have recently shown [1] that the crystalline state of phase change materials is characterized by the occurrence of resonant bonding, a particular flavour of covalent bonding. The concept of resonant bonding leads to an intuitive understanding of the observed material properties, e.g. the approximately octahedral coordination and the polarizability enhancement in the crystalline state. In order to quantify resonance bonding, infrared spectroscopy experiments, i.e. a combination of FTIR-reflectometry and ellipsometry, have been performed. Here, the results of these investigations will be presented.

Key words: phase-change, resonance bonding, crystalline, amorphous, data storage, dielectric function, spectroscopy

1. INTRODUCTION

As phase-change materials [2] attract more and more interest, with their field of application growing towards replacing flash memories, the quest for novel materials becomes ever more demanding. Since a phase-change based device is inherently limited by the properties of the employed phase-change material, a detailed understanding and modeling of phase-change properties is inevitable. However, today's materials result from trial-and-error methods, and only few schemes exist to assist tailoring superior materials. Scientifically, the understanding of prototype materials is generally believed to lead to fundamental models, which in turn help engineers to tailor superior materials and to improve their devices. The scientific challenge of this task is the accumulation of properties that need to be taken into account concurrently. Mainly, a suitable material must exhibit a pronounced optical or electrical contrast between the amorphous and crystalline state. At the same time, the tendency towards crystallization of an amorphous bit must be small at ambient conditions, nevertheless crystallization must proceed rapidly at elevated temperatures. Our focus will be on the first of these requirements. We believe that the key to a general understanding of why certain materials exhibit phase-change properties lies within the crystalline state. The identification of this key property is the subject of this document, which is based on our recent publication [1].

Our discussion will rely on two observations, the first of which concerns the structure. From numerous thorough structural investigations reported in literature, it is evident that the structure of prototype phase-change materials is dominated by three contributions. Generally, the coordination of the atoms is approximately governed by the $8-N$ rule (N being the valence) in the amorphous phase, and six-fold in the crystalline phases. However, local distortions, often referred to as Peierls-distortions, slightly change the bonding in the latter phase, i.e. split up the bonds into long and short ones. As the third contribution, we would like to identify the ordering of sublattice occupations; for instance for GeSb_2Te_4 , a metastable rocksalt-like phase with a statistical occupation of the Ge/Sb/vacancy-sublattice is reported, which transforms into an ordered layer structure upon the transition into the stable crystalline phase. We will combine these findings with the results of our spectroscopic measurements that will be presented in the next section and complete the foundation of our discussion.

2. EXPERIMENTS

Since the optical contrast in reflectivity between crystalline and amorphous state at the wavelength of the employed laser (currently ranging between 1.59eV and 3.06eV) is crucial for optical applications, the dielectric function in the range of typical ellipsometry setups (0.8eV to 5 eV) is routinely determined for all material candidates. In our study, we have extended this range towards smaller wavelengths (0.025 eV) by means of concurrent Fourier transform infrared spectroscopy measurements in reflectance mode. This allows for a precise investigation of the dielectric function in the range of free carrier-contributions and the optical gap, since for typical phase-change materials it is on the order of only 0.5eV in both phases.

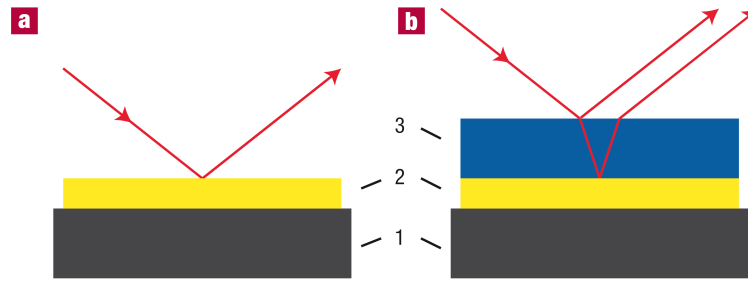


Figure 1: Sample Geometry. (a) A glass substrate (1) covered with a 150nm thick Au-layer (2) serves as a reference sample. (b) A semiconductor film deposited on top (3) can then be investigated in reflectance mode. From [1].

The sample geometry employed is illustrated in Fig. 1. Thick polycrystalline films ($\sim 0.5\mu\text{m}$) of the materials investigated were sputter-deposited onto glass substrates, which were previously covered with 150nm thick Au-layers that work as almost ideal mirrors. The resulting reflectance spectra of these layer stacks were fitted concurrently with the ellipsometry data to a model dielectric function composed of three contributions (for a detailed description please refer to [1]),

$$\varepsilon(\omega) = \varepsilon_{\text{const}} + \varepsilon_{\text{Drude}}(\omega) + \varepsilon_{\text{Tauc-Lorentz}}(\omega)$$

The first, constant term accounts for high-wavelength contributions, the second for Drude-like free-carrier effects (if applicable),

$$\varepsilon_{\text{Drude}}(\omega) = \frac{\omega_p^2}{\omega(\omega + i\gamma)},$$

and the third one for the onset of optical transitions by means of a Tauc-Lorentz oscillator,

$$\text{Im}(\varepsilon_{\text{Tauc-Lorentz}}(\omega)) = \frac{1}{\omega} \frac{S^2 \omega_0 \gamma (\omega - \omega_{\text{gap}})}{(\omega^2 - \omega_0^2)^2 + \omega^2 \gamma^2} \Theta(\omega - \omega_{\text{gap}})$$

3. RESULTS & DISCUSSION

3.1 EXPERIMENTAL RESULTS

The investigation of a number of phase-change materials revealed a generic behavior different from that of a typical four-fold coordinated covalent semiconductor, AgInTe_2 , which was simultaneously studied as a reference. This difference is already evident from the raw reflectance data in the small-wavelength regime (\sim gap) as can be seen in the exemplary measurements shown in Fig. 2 and 3. Only for phase-change materials, a pronounced difference between the phases is observed.

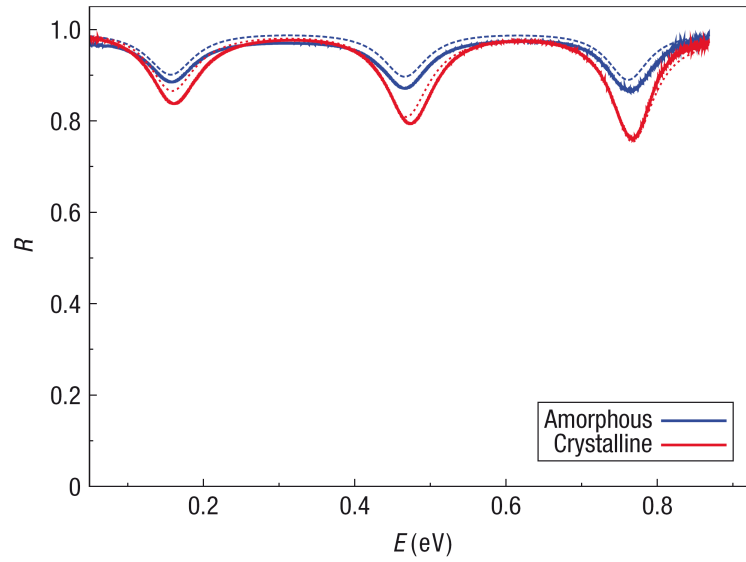


Figure 2: Reflectance of AgInTe_2 . Solid lines show experimental data, dashed lines the simulation. From [1].

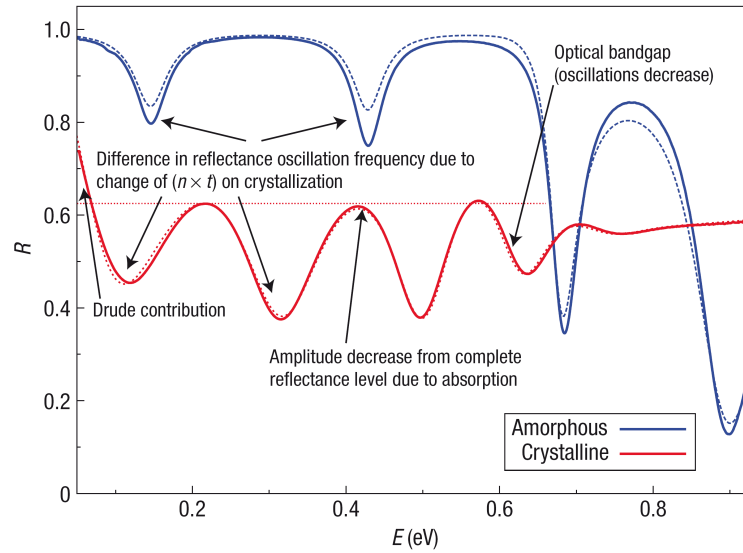


Figure 3: Reflectance of Ge_2SbTe_4 . Solid lines show experimental data, dashed lines the simulation. From [1].

Namely three changes are discernible; as the oscillations vanish at smaller wavelengths in the crystalline case, it is clear that the optical gap becomes smaller. Also, the maximal reflectance values are significantly reduced for the crystal due to absorption via a free-carrier contribution absent in all amorphous samples. Last but not least, the average distance between the fringes decreases significantly. The latter effect is linked to the optical path length, but the density change and therewith the resulting change in film thickness between the phases can not account for that. Instead, the index of refraction must have increased significantly.

Indeed, the results from the fits as listed in Tab. 1 as well as the model dielectric functions compiled in Fig. 4 confirm this conclusion. In fact, the optical dielectric constant ϵ_∞ increases by more than 100% upon crystallization alongside a concurrent decrease of the optical gap by up to 71%. The large absolute values of ϵ_∞ imply that a strongly enhanced polarizability is present in the crystalline state. Thus, we conclude that for the amorphous phase, there is 'ordinary' covalent bonding taking place, while the key to the optical contrast lies within the crystalline state. It will be the scope of the next section to identify why the crystalline state behaves this way.

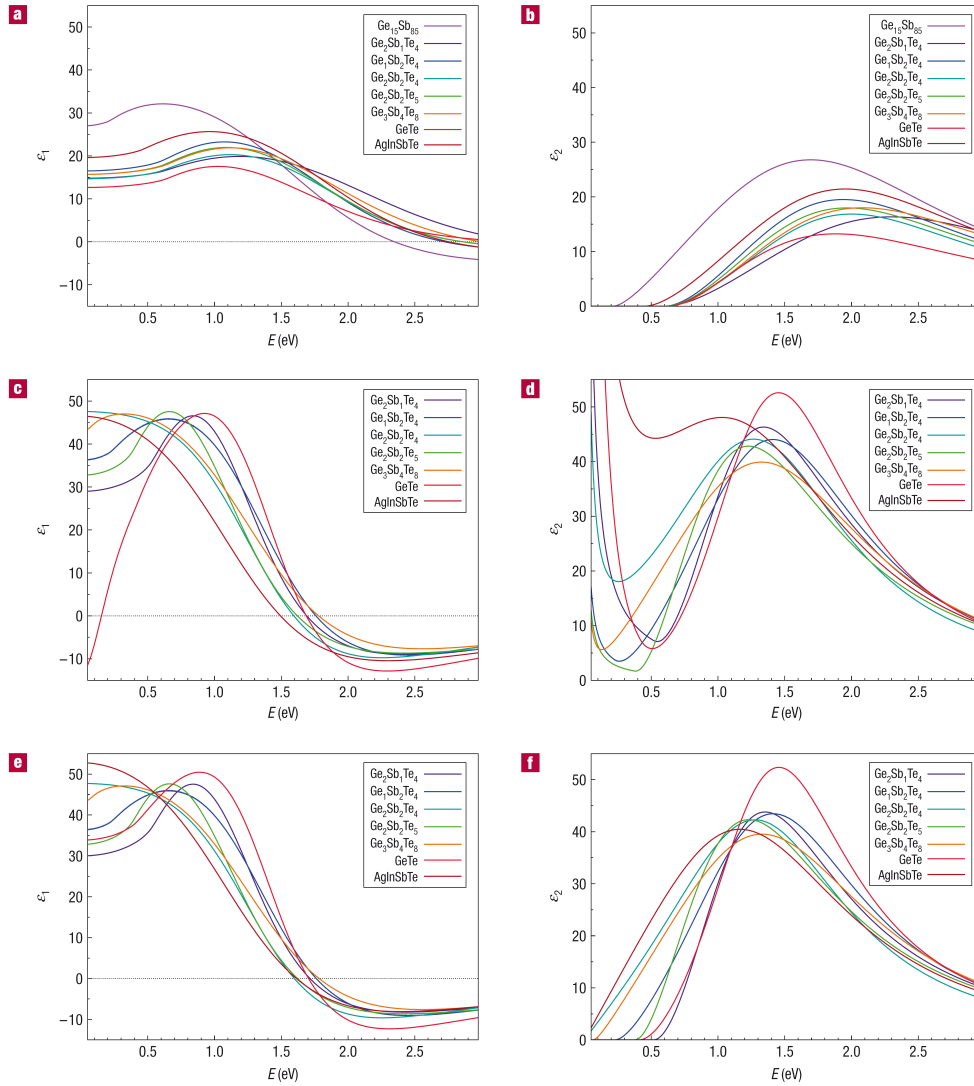


Figure 4: Model dielectric functions. (a),(b) Amorphous phase, (c),(d) crystalline phase, (e),(f) same as (c),(d) but with free-carrier concentration subtracted. From [1].

	ϵ_∞			E_g		
	Amorphous	Crystalline	% increase	Amorphous	Crystalline	% decrease
$\text{Ge}_1\text{Sb}_2\text{Te}_4$	16.6 ± 0.3	36.2 ± 0.9	118	0.76	0.39	49
$\text{Ge}_1\text{Sb}_1\text{Te}_2$	14.8 ± 0.4	47.7 ± 0.8	222	0.77	0.20	74
GeTe	13.2 ± 0.2	33.2 ± 0.8	152	0.78	0.55	35
$\text{Ge}_2\text{Sb}_2\text{Te}_5$	16.0 ± 0.4	33.3 ± 0.8	108	0.77	0.48	29
$\text{Ge}_{15}\text{Sb}_{85}$	26.9 ± 0.7	—	—	0.41	—	—
$\text{Ge}_2\text{Sb}_1\text{Te}_4$	14.5 ± 0.3	29.8 ± 1.6	106	0.80	0.61	24
$\text{Ge}_3\text{Sb}_4\text{Te}_8$	15.6 ± 0.2	43.4 ± 1.2	178	0.79	0.24	70
AlST	19.6 ± 0.5	52.8 ± 1.5	169	0.63	0.18	71

Table 1: Optical dielectric constants and optical gaps. From [1].

3.2 RESONANCE BONDING

As we have noted above, the crystalline structures of phase-change materials are characterized by almost six-fold coordination. But, if we count the number of valence electrons present in these systems, we see that there are not enough in order to establish saturated bonds. Indeed, the distortions strengthen some bonds at the expense of others, making them more saturated. Nevertheless, these distortions are only a perturbation of the fundamental undistorted atomic and electronic structure. So we will first discuss the (hypothetical) undistorted case and will address the role of the distortions later.

The undistorted case can be interpreted along the lines of Pauling [3], Lucovsky/White [4] and Littlewood [5,6]. The systems we deal with have about three p-electrons per atom, so they are almost isoelectronic to group V-elements such as Sb and IV-VI-compounds like GeTe. In both of these material classes, the same structure as exhibited by phase-change materials (save for absent ordering effects) is found. The electronic structure can be understood as a result of resonance bonding, a particular flavor of covalent bonding. This model assumes a complete basis to be composed of all (hypothetical, symmetry-related) saturated bond-configurations. The groundstate is then a superposition of all these basis states, illustrated in Fig. 5. For the undistorted case, no band gap exists unless a sufficiently large polar contribution opens up one. Furthermore, the fingerprint-effect of a system dominated by resonance bonding are large electronic polarizabilities, i.e. large values of ϵ_∞ , just as observed in our measurements. Resonance bonding can only prevail if there is a mid-range order, i.e. only in crystalline structures.

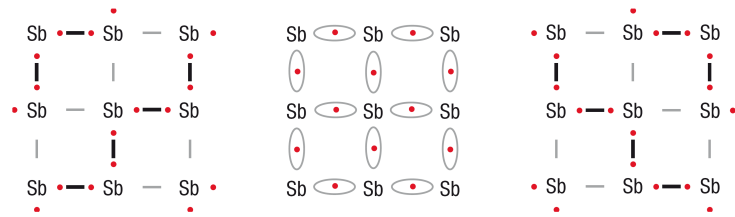


Figure 5: Schematic illustration of resonance bonding for antimony. Shown is the (001)-plane of a hypothetical simple cubic crystal. On the left and on the right two possible saturated-bond configurations are shown. The groundstate results as a superposition of all these states (middle). From [1].

However, such an electronic structure is prone to the occurrence of distortions, which lower the energy of occupied states and open/increase a gap [7,8]. Approximately, the electronic system of a slightly distorted system can still be expressed in the same basis as before, but the mixing coefficients will be different, favoring the formation of less but more saturated, short bonds. In particular, this results in a weakening of the resonance effect, e.g. a decrease of ϵ_∞ , and reduces the contrast between the crystalline and the amorphous phase.

By comparison, we conclude that phase-change materials are very similar to those group V- and IV-VI-materials for which the model of resonance bonding successfully explains the observed electronic properties. The crystalline phases exhibit large optical dielectric constants and the optical gaps are comparably small, in this model resulting from a polar contribution and the local distortions. In turn, we conclude that resonance bonding is a prerequisite for a phase-change material. Its occurrence is what allows phase-change materials to exhibit a substantially different atomic and electronic structure in the crystalline state as compared to the amorphous one. Resonance bonding can prevail in systems with a sufficient number of valence electrons. Local distortions compete with resonance bonding and reduce the contrast.

4. CONCLUSION

We have studied the dielectric function of numerous phase-change materials in both the amorphous and crystalline state by means of combined ellipsometry and Fourier transform infrared spectroscopy. Our experimental investigations have shown that the (poly)crystalline phases of thin films of phase-change materials are characterized by a significant increase in their optical dielectric constant as compared to the amorphous phase. This sets them apart from other semiconductors, which do not show such behavior. The origin of this polarizability enhancement is attributed to the occurrence of resonance bonding. This model allows us to understand both why the chemical bonding changes between the phases, and concurrently the impact on the optical properties. Since this is a generic feature, we conclude in turn that those materials that exhibit resonance bonding in the crystalline state meet the requirements for optical contrast.

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Biography

Dominic Lencer was born in 1980. He studied physics at RWTH Aachen University, Germany, and received his diploma in September 2006. His thesis was conducted at both the Institute of Physics (IA) of RWTH Aachen University as well as in the Department of Engineering and Applied Sciences of Harvard University, advised by Professor Matthias Wuttig and Professor Frans Spaepen. He was concerned with crystallization kinetics and *ab initio*-modeling of phase-change materials. Since October 2006, he continues his research as a PhD-student in Professor Wuttig's group.