P H Y S I C A L   R E V I E W   L E T T E R S

Origin of the Optical Contrast in Phase-Change Materials

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(Received 25 August 2006; published 6 June 2007)

Several chalcogenide alloys exhibit a pronounced contrast between the optical absorption in the metastable rocksalt and in the amorphous phase. This phenomenon is the basis for their application in optical data storage. Here we present *ab initio* calculations of the optical properties of GeTe and $Ge_1Sb_2Te_4$ in the two phases. The analysis of our computations and experimental data reveal the correlation between local structural changes and optical properties as well as the origin of the optical contrast in these materials. We find that the change in optical properties cannot be attributed to a smearing of transition energies as commonly assumed for amorphous semiconductors: the optical contrast between the two phases can only be explained by significant changes in the transition matrix elements.

Tellurides containing Ge and Sb such as $Ge_1Sb_2Te_4$ and $Ge_2Sb_2Te_5$ are characterized by a fast and reversible phase transition from the metastable, crystalline (*c*) phase to the amorphous (*a*) phase. This transformation is accompanied by a profound change of electrical conductivity and optical reflectivity [1–3]. The pronounced optical contrast in phase-change materials (PCM) such as GeSbTe alloys is employed in optical data storage, e.g., in rewritable DVD's. The change in electrical properties—e.g., the resistivity change—is one of the crucial features that would be used in phase-change random access memories, a very promising candidate for future nonvolatile memories [4,5]. Conventional covalent semiconductors such as Si, Ge, or III-V alloys behave very differently; in particular, they do not exhibit such a strong optical contrast [6]. A recent remarkable observation provided some clues to the origin of this effect. Extended x-ray-absorption fine structure spectroscopy (EXAFS) studies of the local order of $Ge_2Sb_2Te_5$ as well as GeTe showed a marked change of short-range order upon crystallization of the *a* state [7,8]. Such a finding is not observed for conventional covalent semiconductors, suggesting that the short-range structural rearrangement could be closely related to the optical contrast. However, the change in optical properties upon amorphization of the PCM is still far from being understood. Experiments can show trends, but it is difficult to correlate from experiment alone a macroscopic measurement, like the optical properties, with microscopic details, like the local atomic structure. First principles calculations provide an ideal complementary tool in this study as structural models with different local order can be explored. We have hence performed a joint experimental and numerical study in order to elucidate several major questions, in particular, (i) can a change in local order explain the strong optical contrast in PCM's? (ii) Is this contrast governed by the corresponding change of the electronic energies (the joint density of states)? (iii) Can a simple and general

model reproduce this phenomenon so that the results could be used in the search for improved materials?

The experimental data presented here were obtained for magnetron sputtered thin films (150–250 nm) of GeTe and $Ge_1Sb_2Te_4$ on glass. The measurements—performed at room temperature—include Fourier transform infrared spectroscopy and ellipsometry in the combined energy range of 0.1–5.4 eV.

Density functional theory calculations of the electronic ground state of GeTe and $Ge_1Sb_2Te_4$ were performed with the code ABINIT [9,10], using norm-conserving pseudopotentials [11], and a generalized gradient approximation [12] for the exchange-correlation potential. The *c* phases exhibit a rocksalt structure where Te atoms occupy one sublattice, while the second one is occupied either by Ge atoms (in GeTe) or by Ge/Sb atoms and 25% of vacancies (in $Ge_1Sb_2Te_4$) [13,14]. The atomic positions in the *c* phase were relaxed, resulting in a rocksaltlike structure with local distortions as reported recently [7,15]. The *a* states were studied in a supercell configuration containing 56 atoms ($Ge_1Sb_2Te_4$) and 64 atoms (GeTe), respectively. Based on the observation that in *a* GeTe a fraction of Ge atoms occupies tetrahedrally coordinated positions [8] instead of the octahedral environment in the *c* phase, we constructed simple structural models: In a supercell containing 64 atoms (32 Ge and 32 Te atoms) in octahedral coordination 2, 4 and 8 Ge atoms are displaced into tetrahedrally coordinated positions in order to obtain different models for the *a* state. For $Ge_1Sb_2Te_4$ two simple models were used for the same purpose: in one model all eight Ge atoms exhibit tetrahedral coordination (am_1) in accordance with earlier EXAFS results [7]. In order to test the possibility of a mixture of short-range order as found in *a* GeTe, in the second model 4 Ge atoms remain octahedrally coordinated and 4 become tetrahedrally coordinated (am_2). The models used here still exhibit long-range order, which should not be present in the *a* state. However, in

covalent materials the optical properties are mainly defined by short ranged nearest-neighbor interactions. In order to study the correlation between the unusual changes in short-range order and the optical properties it is thus well justified to neglect the change in long-range order upon amorphization. The chosen structural models are expected to reproduce the experimentally observed density decrease of 5%–10% [16–18] upon amorphization. Our calculations yield a decrease of 4.8%–9.8% for the amorphous models, consistent with these experimental values.

The optical properties were calculated within time-dependent density functional theory using the code DP [19]. For small-gap semiconductors like the materials studied here, self-energy and excitonic effects can be taken into account by replacing Kohn-Sham eigenvalues with quasiparticle energies calculated within the *GW* approximation for the self-energy [20], and by using a model long-range exchange-correlation kernel $f_{xc} = -\alpha/q^2$ simulating the electron-hole interaction [21,22]. Since the calculated dielectric constant ϵ_0 takes values between 30 and 76 for the systems considered here, screening is very large and, consequently, the excitonic contribution is negligible, i.e., $\alpha = 0$. Hence the random phase approximation (i.e., $f_{xc} = 0$), using *GW* quasiparticle energies instead of Kohn-Sham eigenvalues represents the best approximation to simulate many-body effects in GeTe or $Ge_1Sb_2Te_4$. The *GW* corrections to the quasiparticle band structure of the *c* systems in their primitive unit cells give a blueshift of the absorption threshold of 0.15 eV for GeTe and of 0.1–0.2 eV for $Ge_1Sb_2Te_4$. We take the same shifts for the corresponding amorphous phases, since *GW* corrections can be assumed to depend weakly on the local structure (see, e.g., [23]).

In Fig. 1 our experimental (a) and calculated spectra (b) + (c) are presented. The experimental data are in line with measurements of PCM's such as $Ge_1Sb_2Te_4$, $Ge_2Sb_2Te_5$, or $Ge_1Sb_4Te_7$ found in the literature [24,25]. The optical contrast between the *c* and the *a* state is mainly caused by two features: Primarily, the absorption in the *a* state decreases and broadens significantly in both alloys. Furthermore a blueshift of the spectra is observed upon amorphization. The experimental spectrum of the *c* state of GeTe exhibits a Drude peak at energies below 0.5 eV. The metallic *p*-type conductivity inducing this peak stems from unoccupied states at the valence band edge [26], which are due to Ge vacancies. Such vacancies are known to be the dominant point defects in *c* GeTe (see, e.g., [27]). For the comparison between theory and experiment it should be kept in mind that calculations are performed for a bulk single-crystalline solid, and measurements on thin films. In view of that, quantitative deviations between calculated and experimental spectra of the *c* phases may occur.

Figure 1(b) shows calculations of the unrelaxed (i.e., the perfect rocksalt phase with six nearest neighbors) and the relaxed *c* GeTe as well as of a relaxed structure containing a Ge vacancy. The first spectrum is very different from the
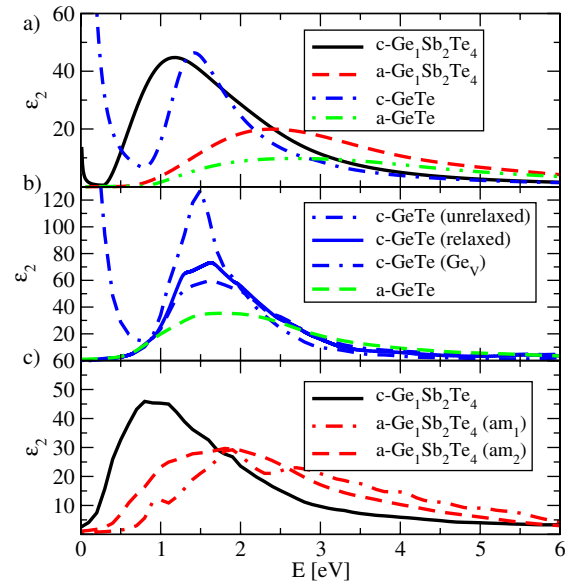

FIG. 1 (color online). Optical absorption of GeTe and $Ge_1Sb_2Te_4$ (a): experimental, (b) + (c): calculation, here two amorphous models for $Ge_1Sb_2Te_4$ are displayed. For both alloys a decrease, a broadening and a blueshift of the absorption, is reproduced for the *a* state. Lattice distortions upon structural relaxation and Ge vacancies lead to a better agreement with the experiment in *c* GeTe.

experiment, the second one is considerably improved while the last shows good agreement with the experiment. Most notably the Drude peak is well reproduced now. Furthermore, the intensity of the main peak decreases and thus approaches the experimental value. If vacancies are considered in the *a* state, a similar decrease of the absorption intensity can be observed (not shown here). The three employed models for the *a* state yield similar spectra. Therefore only one model (with 4 Ge atoms occupying tetrahedral positions) is shown in Fig. 1. The peak of the absorption spectrum is found at the same energy in the *c* and *a* state, however the overall spectral weight exhibits a blueshift in the *a* state. Similarly to the experiment, the spectrum broadens and decreases in intensity upon amorphization. Note that both effects, the incorporation of vacancies as well as the local order change from octahedral to tetrahedral coordination, reduce the number of Ge-Te bonds.

For $Ge_1Sb_2Te_4$ [Fig. 1(c)] both contributions to the optical contrast —the decrease and broadening of the spectrum as well as the blueshift- are reproduced for both amorphous models. The absorption spectrum of am_1 is more structured than the experimental spectrum. However, this might be due to the fact that this model still exhibits long-range order, which is obviously not present in the experiment. The lifting of long-range order should result in less well-defined transition energies and thus in a smearing of the absorption spectrum. Since both models successfully describe the optical contrast due to short-range changes between the *c* and the *a* state, in the follow-

ing analysis am_2 will be employed without loss of generality.

Further structural rearrangements, not captured by our simple structural models, certainly lead to further modifications of the spectra. However, the pronounced change of the calculated spectra provides an unambiguous answer to (i): the shift of Ge atoms to tetrahedral positions, i.e., the change in the local order of the Ge atoms upon amorphization, is the dominant effect in the generation of the optical contrast.

In the following discussion we will focus on a deeper study of the origin of this optical contrast induced by the change in the local order. As we have verified, crystal local field effects only play a very minor role in the spectra [28] and, as we have pointed out above, self-energy corrections are small. We can therefore base our analysis of the absorption results on Fermi's golden rule in the independent-particle approximation (see, e.g., [29]) within the Kohn-Sham picture. This approach enables us to isolate the contributions to absorption of matrix elements and energy levels (ε_i). This separation is essential to answer (ii). In this approximation the imaginary part of the macroscopic dielectric function

$$\epsilon_2(\omega) = 2\frac{4\pi^2}{\Omega N_\mathbf{k}\omega^2}\lim_{\mathbf{q}\to 0}\frac{1}{\mathbf{q}^2}\sum_{v,c,\mathbf{k}}|\mathbf{q}\cdot\mathbf{m}_{v,c,\mathbf{k}}|^2$$
$$\times\,\delta(\varepsilon_{c\mathbf{k}} - \varepsilon_{v\mathbf{k}} - \omega), \tag{1}$$

where Ω is the volume of the cell and $N_\mathbf{k}$ the number of k points, is governed by the joint density of states (JDOS/$\omega^2 \equiv \frac{1}{N_\mathbf{k}\omega^2}\sum_{v,c,\mathbf{k}}\delta(\varepsilon_{c\mathbf{k}} - \varepsilon_{v\mathbf{k}} - \omega)$) and by the velocity (**v**) matrix elements of the optical transitions $\mathbf{m}_{v,c,\mathbf{k}} \equiv \langle c|\mathbf{v}|v\rangle$. Figure 2(a) presents the JDOS/ω^2 for $\mathrm{Ge_1Sb_2Te_4}$ and 2(c) presents the JDOS/ω^2 for GeTe. In $\mathrm{Ge_1Sb_2Te_4}$ up to 1.4 eV the JDOS in the c phase is stronger than in the a state, while above 1.4 eV a larger number of transitions is found in the a state. On the other side the absorption spectrum in the c phase exhibits a higher intensity up to 1.8 eV (Fig. 1). Hence, assuming constant matrix elements the JDOS cannot explain the optical contrast between the two phases. In GeTe the JDOS is even less suitable to explain the optical contrast: up to 1.7 eV the JDOS is larger in the a state, for higher energies it is very similar in both phases. With constant matrix elements one would therefore expect an absorption spectrum showing higher intensity in the a state up to 1.7 eV and very similar spectra for both phases above this value. However, this is clearly not the case in the measured and calculated absorption spectra (see Fig. 1). Thus in both alloys the optical contrast can only be understood if the contribution arising from changes in the oscillator strength of the optical transitions is taken into account. This contribution is shown in Fig. 2(b) ($\mathrm{Ge_1Sb_2Te_4}$) and 2(d) (GeTe). For $\mathrm{Ge_1Sb_2Te_4}$ up to about 2 eV stronger matrix elements are found in the c phase, for c GeTe they are significantly stronger in the entire spectral range. For GeTe we have also included the
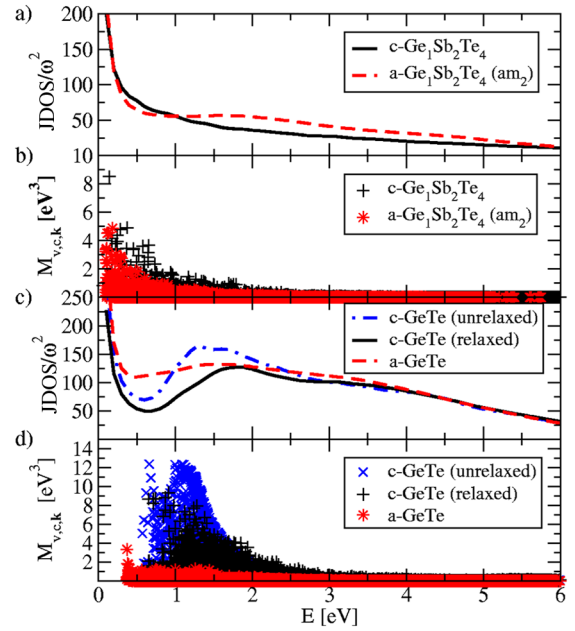

FIG. 2 (color online).   (a) JDOS/ω^2 of $\mathrm{Ge_1Sb_2Te_4}$ in the c- and the a state in number of transitions/eV^3 per cell and k point. Up to 1.4 eV the JDOS in the c phase is stronger than in the a state, while ϵ_2 is stronger in the c phase up to 1.8 eV. For GeTe (c) up to 1.7 eV more transitions are found in the a state compared to the relaxed c phase. For both materials the decrease in the absorption upon amorphization can only be explained taking into account the velocity matrix elements shown in (b) ($\mathrm{Ge_1Sb_2Te_4}$) and (d) (GeTe) with $M_{v,c,\mathbf{k}} = 2\frac{4\pi^2}{\Omega}\lim_{\mathbf{q}\to 0}\frac{1}{\mathbf{q}^2}|\mathbf{m}_{v,c,\mathbf{k}}|^2$.

values relative to the undistorted phase, where the oscillator strength is even stronger. As the change in oscillator strength is larger in GeTe compared to $\mathrm{Ge_1Sb_2Te_4}$, the difference in the intensity of the absorption spectra of the c and the a state is more pronounced for GeTe as well. This result of the calculation is also present in the experimental spectra in Fig. 1. Hence Figs. 2(a)–2(d) show that the optical contrast between the c and a state of GeSbTe alloys are dominated by changes of the matrix elements, providing an unexpected answer to question (ii). In fact, this result is in striking contrast to the common explanation of the "moderate" changes in the optical absorption upon amorphization of tetrahedral semiconductors such as Si, Ge, or the III-V compound GaAs. These are explained by a smearing of the JDOS resulting from the loss of long-range order and the formation of defect states in the gap in the a state [6]. Thus the unusual change in the local order in PCM's upon amorphization induces another remarkable effect, namely, a significant decrease of the oscillator strength of the optical transitions.

Further studies reveal that this decrease can be mainly attributed to a change in the spatial overlap of the wave functions which contribute to the optical transitions. Figure 3 shows the number of matrix elements plotted against the overlap $\int|\phi_c(\mathbf{r})||\phi_v(\mathbf{r})|d\mathbf{r}$. For both alloys the curves show similar behavior, shifting towards lower
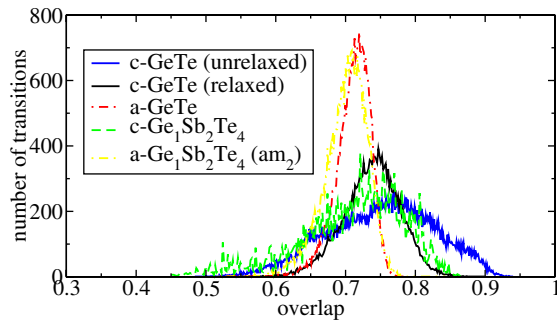
FIG. 3 (color online). The number of matrix elements for excitation energies up to 2.5 eV vs the overlap $\int |\phi_c(\mathbf{r})||\phi_v(\mathbf{r})|d\mathbf{r}$.

values in the a-state and thus indicating a weaker overlap. These results provide a simple model suitable to answer question (iii). The optical properties in PCM's are governed by two effects: the change from octahedral to tetrahedral coordination as well as the inclusion of vacancies reducing the number of Ge-Te bonds and thus the total oscillator strength. Moreover, the change of the local geometry upon amorphization or distortion leads to a change in the overlap of the wave functions, resulting in smaller individual matrix elements. This explains the decrease of the absorption upon distortion, vacancy inclusion as well as amorphization thus providing interesting hints for optical data storage applications: As both the change from octahedral to tetrahedral coordination as well as the inclusion of vacancies reduce the number of Ge-Te bonds optical properties in PCM's can be tuned by modifying these two contributions. In particular the latter property is easily accessible. As has been shown recently [30], the vacancy concentration in PCM's can be controlled over a wide range. Furthermore, [30] shows that the absorption in the c state decreases with the degree of distortions (which again can be tuned by changing the stoichiometry).

In summary we provide an explanation for the change of the optical absorption upon amorphization in PCM's and reveal the reason of differences in the optical properties of GeTe and $Ge_1Sb_2Te_4$. The changes in the number of bonds and in the local order upon amorphization result in significant changes of the oscillator strength which in turn result in the unusually pronounced optical contrast between the c and the a state. Thus they differ significantly from simple tetrahedral semiconductors such as Si or Ge, which retain the local order in the a state and therefore exhibit only minor changes in their optical properties. Besides providing fundamentally new insight in the physics of the optical absorption of amorphous materials, our results reveal important trends for a systematic material optimization of phase-change alloys.

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