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Correlation between optical absorption redshift and carrier density in phase change materials

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Here, we report an optical absorption redshift map for GeTe-Sb₂Te₃ pseudo-binary alloys. We found that, with phase change from amorphous to crystalline, the observed redshift increases with Ge concentration along pseudo-line of compositions, which directly reflects the enhanced electron delocalization/resonant bonding and increased carrier concentrations in the respective crystal compounds. The measured valence band maximum shift towards the Fermi energy from amorphous to crystalline phase supports the observed similar trend in redshift and carrier density. We show that the correlation between optical redshift and carrier density, attributed to the resonant bonding, can be rationalized by calculating the valence electron concentration, the ionicity, and hybridization. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4822311>]

I. INTRODUCTION

Chalcogenide based phase change materials, especially Ge-Sb-Te (GST) alloys along the GeTe-Sb₂Te₃ pseudo-binary line, exhibit pronounced optical and electrical contrast with rapid phase transition from amorphous to crystalline phase. This makes them suitable candidates for rewritable optical storage media^{1,2} and phase change random access memory.^{3,4} Hence, much effort have been undertaken to understand the properties of these materials as well as the origin of the large contrast in properties between the phases. For example, both Park *et al.*⁵ and Shportko *et al.*⁶ measured the dielectric functions of amorphous and crystalline GST thin films to determine its optical band gap energies and electronic polarizability, respectively. The large optical contrast in GST is attributed to the resonant bonding within the crystalline phase, which is evidenced by the enhancement in the electronic polarizability of the crystalline phase. A two axis map showing hybridization (r_{π}^{-1}) and ionicity (r_o) has been proposed by Lencer *et al.*,⁷ which indicates that phase change materials lie in a limited area of low ionicity and hybridization, where resonant bonding prevails. Apart from optical properties, GST charge transport properties such as the carrier density, have also been investigated.⁸⁻¹⁷ These alloys are reported to be *p*-type semiconductors with a very high hole concentrations¹⁰ of over 10^{20} cm^{-3} . It has been pointed out that carrier concentrations are not a consequence of the small gaps and thermal excitation, but are induced by a pronounced down-shift of the Fermi level, or valence band maximum up-shift.¹⁸ This indicates that states around the Fermi level and their nature dominate the electrical behavior

of the phase change materials. Despite many investigations focused on characterizing the optical and electrical properties of phase change materials separately, there is still a lacking of understanding on the direct relationship between them.

Recently, we observed an unique optical absorption redshift in the phase change material Sb₂Te₃, as it undergoes an amorphous to crystalline phase transition.¹⁹ Delocalized electrons arising from resonant bonds in the crystalline phase change material were reported to be responsible for this redshift. In this work, we extend this previous investigation to GST family and quantitatively study the relationship between redshift and Ge concentration in GeTe-Sb₂Te₃ pseudo-binary alloys. We examine the bond resonance in phase change pseudo-binary alloys, from Sb₂Te₃ to GeTe, by measuring the optical absorption peak redshift, and found that it exhibits a similar trend as the charge carrier density. We then invoke the concept of valence electron concentration (VEC) to associate the trends in these two properties and confirm the relationship between the redshift and carrier density by contrasting the amorphous and crystalline valence band spectra, measured by X-ray Photoelectron Spectroscopy (XPS).

II. EXPERIMENTAL

Amorphous phase change thin films, GeTe, Ge₂Sb₂Te₅, GeSb₂Te₄, GeSb₄Te₇, and Sb₂Te₃, were deposited on quartz substrates at room temperature by DC sputtering. The crystalline samples were obtained by annealing the as-deposited samples to 300 °C for 5 min in vacuum. We then used XPS to confirm the films compositions and to measure the valence band spectra of the as-deposited and annealed phase change films. The transmittances (T) of both amorphous and

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crystalline films were characterized using ultraviolet-visible-near-infrared spectrophotometer at room temperature for wavelengths ranging from 200 nm to 800 nm. Nano films 20 nm, 30 nm, and 60 nm are used for the transmittance measurements. Hall conductivity measurements of the crystalline films are performed to determine the carrier density. We confirm that all samples used in this work are phase change materials and suitable for redshift studies by studying its crystallizing temperature (real-time measurement of the film's reflectivity and resistance during annealing). The crystallizing temperature measured for each film increases with increasing Ge concentration, which are in agreement with previous reports.²⁰⁻²²

III. RESULTS AND DISCUSSION

The optical absorption spectra of the amorphous and crystalline phase change films were derived from the transmittance spectra of two different thickness films. The optical absorption coefficient (α) can be calculated using the relation¹⁹

$$\alpha = \left(\frac{1}{d_2 - d_1} \right) \ln \left[\frac{T_1(\lambda)}{T_2(\lambda)} \right], \quad (1)$$

where d_i is the thickness of the measured film and $T_i(\lambda)$ are the transmittance of film i ($i = 1, 2$) in various wavelengths. Figure 1 shows the absorption spectrum of the thin films (Sb_2Te_3 , GeSb_4Te_7 , GeSb_2Te_4 , $\text{Ge}_2\text{Sb}_2\text{Te}_5$, and GeTe) in the amorphous and crystalline phase as a function of wavelengths. From the absorption peaks of the amorphous and crystalline phases of Sb_2Te_3 , one can note a redshift of 105.53 nm from the amorphous to crystalline phase.

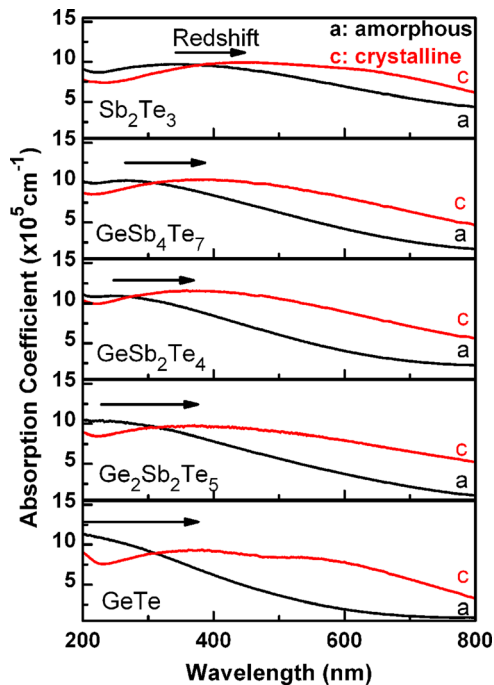


FIG. 1. Optical absorption coefficient of amorphous and crystalline phases as a function of wavelength for $\text{GeTe-Sb}_2\text{Te}_3$ pseudo-binary alloys. Arrows indicate the redshift observed in the absorption peak from amorphous to crystalline phases.

TABLE I. Summary of the optical absorption peak positions for $\text{GeTe-Sb}_2\text{Te}_3$ pseudo-binary alloys.

Phase change material	Absorption peak position				Redshift (nm)
	Wavelength (nm)		Energy (eV)		
	Amorphous	Crystalline	Amorphous	Crystalline	
Sb ₂ Te ₃	342.13	447.66	3.63	2.77	105.53
GeSb ₄ Te ₇	264.76	386.87	4.69	3.21	122.11
GeSb ₂ Te ₄	247.18	369.50	5.02	3.36	122.32
Ge ₂ Sb ₂ Te ₅	228.35	376.01	5.43	3.30	147.66
GeTe	<200	376.66	>6.20	3.29	>176.66

Similarly, all other crystalline phase change films also show a redshift in the absorption peak with respect to its amorphous state. It should be noted that the absorption is also dependent on the crystal orientations of the films. Hence, differences in method of deposition and the orientation of the substrates will slightly affect the absorption spectra.¹⁹ Here, all films were deposited on quartz substrate and annealed under the same conditions for absorption studies.

Table I summarizes the measured position of the optical absorption peak for both amorphous and crystalline phase change films and its corresponding redshift $\Delta\lambda$ defined as

$$\Delta\lambda = \lambda_c - \lambda_a, \quad (2)$$

where λ_a and λ_c are the wavelength of the amorphous and crystalline absorption peaks, respectively. As shown in Table I, the redshift increases for increasing Ge concentrations. This is illustrated in Fig. 2(a). As the amorphous GeTe absorption peak is beyond the measurement range, we estimated its redshift to be above 176.66 nm. The redshift

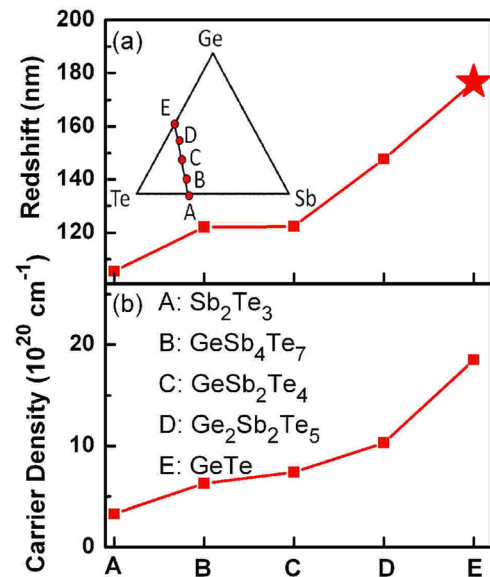


FIG. 2. Redshift and carrier density for $\text{GeTe-Sb}_2\text{Te}_3$ pseudo-binary alloys. (a) Redshift measured from data in Fig. 1 for each respective alloy. The redshift for GeTe , indicated by the star symbol, is an estimated point. (b) Carriers density of respective crystalline phase change films derived from Hall Effect measurements.

increase with Ge concentrations has a similar trend as the crystallizing temperature along the composition line.

It is known that the large optical and electrical contrast between amorphous and crystalline states of a phase change material can be attributed to the significant change in bonding from covalent bonding (amorphous) to resonant bonding (crystalline).²³ The resonant bonding in crystalline phase change materials is caused by pronounced electron delocalization.¹⁸ With the increase in electron delocalization, the energy gap between the valence band and the conduction band decreases (implying smaller excitation energy needed by a photon to excite an electron), causing the optical absorption peak to move to a longer wavelength.²⁴ Therefore, the measured shift of the crystalline optical absorption peak to a longer wavelength with respect to its amorphous counterpart (redshift) is an evidence of resonant bonding existing in crystalline phase change materials.

To obtain carrier density in the alloys, we perform Hall Effect conductivity measurements.^{25,26} The carrier density of the films is plotted in Fig. 2(b) for all films considered which is consistent with previous reports.^{10–17} From Fig. 2(b), the carrier densities increase with increasing Ge concentrations. It is interesting to note that this trend is similar to the measured absorption redshift, which further proves that there may be some correlations between the electron delocalization, and optical and electrical behaviors in the GST crystalline compounds.

In order to understand the relationship between the redshift (directly caused by electron delocalization) and the carrier density in GST, we use the concepts of (VECs)^{21,27,28} in which Wuttig *et al.*²¹ demonstrated that the decrease of the valence electron concentration (by including vacancies) results in a lower charge carrier density in GST alloys. We then linked the VEC with the intrinsic materials property parameters proposed by Lencer *et al.*,⁷ whereby the hybridization and ionicity indicate the resonance character of the GST alloys. He pointed out that the resonance character is weakened both by increasing hybridization and ionicity. Figure 3 shows the calculated VEC with vacancies included, and its relationships with the ionicity (r_σ)⁷ and hybridization (r_π^{-1})^{7,29} of crystalline GST alloys. It can be seen that both ionicity r_σ and hybridization (r_π^{-1}) decrease with an increase in VEC (by including vacancies) in the respective alloys, which means that the weaker/stronger resonant bonding the lower/higher the carrier density in GeTe-Sb₂Te₃ pseudo-binary alloys. Further shown in Fig. 3, the VEC (by including vacancies) increases with Ge concentration, which is consistent with the Hall Effect measurements in Fig. 2(b). Despite the relationship between the VEC and the carrier concentration, we have shown here, one should note that VEC may not be the only contributing factor to the carrier concentration.^{21,30–32} As both the ionicity (r_σ) and hybridization (r_π^{-1}) of the materials affect the degree of resonant bonding, this explains the observed optical absorption shift from amorphous to crystalline phase. In Fig. 3, both r_σ and r_π^{-1} are highest in value for Sb₂Te₃, which is consistent with Fig. 2(a) showing the lowest redshift for Sb₂Te₃. Thus, the larger redshift suggests that the stronger the pronounced electron delocalization/resonant bonding.

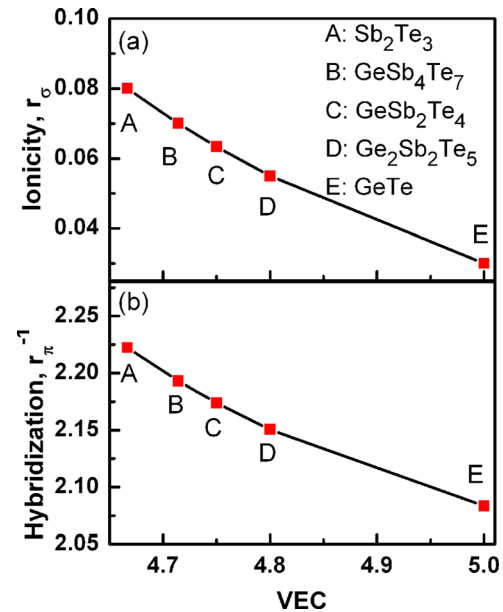


FIG. 3. Ionicity (r_σ) and hybridization (r_π^{-1}) as a function of VEC for GeTe-Sb₂Te₃ pseudo-binary alloys.

Furthermore, we confirmed the redshift observations by contrasting the amorphous and crystalline valence band spectra as shown in Fig. 4. All crystalline GST show a shift in its valence band maximum towards the Fermi energy, that is, a decrease in the band gap energy due to phase change from amorphous to crystalline phase.³³ This explains the redshift of the absorption spectra in crystalline phase relative to its amorphous phase.^{33,34} From Fig. 4, we also observed that the valence band in the amorphous phase is 0.17 to 0.34 eV below the Fermi Level, which means that the Fermi level is close to middle of the gap in the amorphous phase.^{33,34} Moreover, a

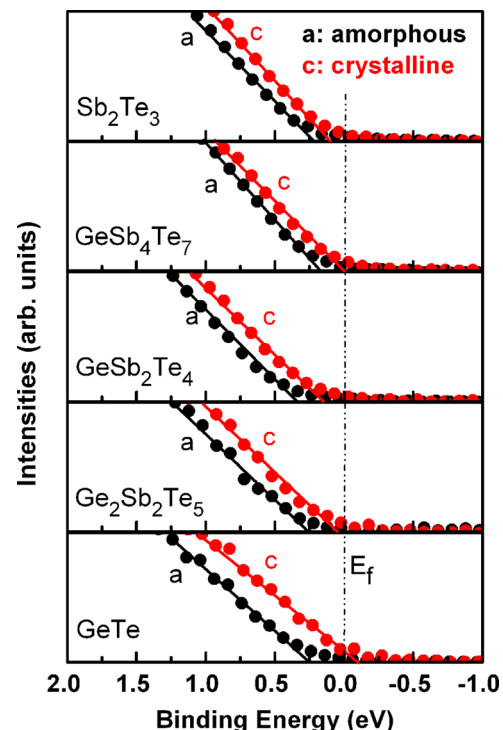


FIG. 4. Valence band spectra for GeTe-Sb₂Te₃ pseudo-binary alloys.

shift of the valence band maximum towards the Fermi level also indicates an increase in hole concentration or carrier density.³⁴ Therefore, the valence band spectra as shown in Fig. 4 support both the absorption redshift and increased carrier concentrations resulting in the crystalline phases.

IV. CONCLUSIONS

In summary, we determined the optical absorption spectra of various amorphous and crystalline phase change materials in the GeTe-Sb₂Te₃ pseudo-binary family. All crystalline films showed a redshift in the optical absorption coefficient peak with respect to its amorphous phase. Hall measurement indicates that the carrier concentration also increases with increasing Ge concentration, similar to the absorption redshift trend. As indicated by XPS spectra, the valence band maximum of the crystalline phase is shifted closer to the Fermi level in comparison to the amorphous phase. This supports the absorption redshift and increased carrier concentrations in the crystalline phases. The calculated VEC (by including vacancies), r_σ and r_π^{-1} of the alloys suggests that the more pronounced the resonant bonding (the larger the redshift), the higher the charge carrier density. Therefore, the degrees of resonant bonding, which can be accessed readily by measuring the redshift, affect both the optical and electrical properties of phase change materials. That suggests that the redshift is a convenient tool in the characterization and search of new phase change materials.

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