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Contrast in terahertz conductivity of phase-change materials

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ABSTRACT

Time-domain terahertz spectroscopy was used to study the dielectric and conductive properties of thin films of four phase-change materials: GeTe, $GeSb_2Te_4$, $GeSbTe_2$, and AgInSbTe. Both amorphous and crystalline phases were studied, and the spectra were analyzed by a model including a harmonic oscillator and the Drude term. Spectra in the crystalline phase of AgInSbTe are dominated by free-carrier motion with a scattering time of 50 fs. In the Ge-containing compounds, we observed a phonon mode and a conductive contribution of free charge carriers with a much shorter scattering time. The conductivity appears to be linked to the distortions of the crystal unit cell from cubic symmetry.

1. Introduction

In recent years, there has been a growing interest in the research of so-called phase-change materials (PCMs) [1]. These materials include germanium telluride (GeTe), related ternary chalcogenide alloys $Ge_xSb_yTe_z$, $In_xSb_yTe_z$, and quaternary non-stoichiometric systems such as $Te_wAs_xSi_yGe_z$ [2] or $Ag_wIn_xSb_yTe_z$ [3]. PCMs represent a class of solids with many interesting properties; they feature reversible phase transitions between amorphous and (metastable) semiconducting crystalline states occurring within times of the order of nanoseconds [4–6]; the speed of crystallization is so high that the semiconducting phases occur in a polycrystalline state. The marked contrast of the optical refractive index [7] and of the conductivity [8] between the phases makes PCMs very attractive for existing and future applications, such as optical data storage devices (e.g. rewritable CDs and DVDs), so-called phase-change memories (PCRAMs), and others. The phase switching is triggered thermally; optical devices make use of focused laser pulses while electrical ones rely on electrical pulses. Upon progressive annealing, a metal–insulator transition can be observed [9].

Along with the technological challenges to be solved in view of application developments, the understanding of the physical mechanisms occurring in PCMs is still incomplete. On the one hand, the main open issue is that of the switching mechanism and its relation to both structure and stoichiometry. On the other hand, the conduction mechanism is still not completely understood, even though the DC conductivity is a property of prime importance for applications of PCMs. While the DC conductivity values in the various phases typically differ by several orders of magnitude, the contrast of the refractive index around the visible region amounts typically to tens of per cent [10].

Various spectroscopic methods have been employed to study optical properties of PCMs. In the mid-infrared region, spectrophotometry was used to measure the transmittance of selected materials from the $Ge_xSb_yTe_z$ system [11]. The experimental data were successfully interpreted in terms of a Drude-type plasma of free carriers; it was found that the main increase of the optical constants occurs in the far-infrared domain. Consequently, the terahertz (THz) time-domain spectroscopy appears to be a very convenient experimental tool for studying directly the dynamic conductivity of PCMs. As the main advantage, it is able to access the frequencies where the most prominent changes of conductivity occur; moreover, it makes it possible to measure the complex optical constants directly without the need either to assume a particular model of the dielectric function or to apply Kramers–Kronig relations.

In this paper, we present a comparative study of four different PCMs in the THz frequency domain; the simplest one is GeTe, which, in the crystalline state, is a well-known ferroelectric; its temperature-dependent THz spectra were recently studied and analyzed in view of the open question about the nature of the ferroelectric phase transition [12]. We performed measurements of the complex transmittance of GeTe and of three other materials in both amorphous and crystalline phases.

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Table 1
Summary of transition temperatures found using DSC, annealing temperatures (applied in measurements to reach the crystalline phases) and densities of the individual phases.

Material	Phase	Transition temperature (°C)	Annealing temperature (°C)	Density (g cm^{-3})
AIST	Amorphous	–	–	6.22
	Hexagonal	160	200	6.56
GeTe	Amorphous	–	–	5.48
	Rhombohedral	210	250	6.24
GST112	Amorphous	–	–	5.84
	Distorted rock salt	181	200	6.48
	Hexagonal	338	370	6.59
GST124	Amorphous	–	–	5.90
	Distorted rock salt	144	200	6.22
	Hexagonal	263	300	6.33

Table 2
Values of parameters from Eqs. (1) and (2) used to obtain the curves shown in Figs. 1 and 2. The stars denote parameters the values of which were fixed in the fitting procedure.

Material	Phase	f (s^{-2})	Γ (THz)	ω_0 (THz)	τ (fs)	σ_{dc} ((Ω cm)$^{-1}$)
AIST	Amorphous	27	3*	1.9	–	–
	Hexagonal	135*	3*	1.9*	55	820
GeTe	Amorphous	70	3*	2.5*	–	–
	Rhombohedral	1×10^3	3*	2.5	3*	1400
GST112	Amorphous	70	2.1	2.2	–	–
	Distorted rock salt	370	2.0	2.0	3*	90
	Hexagonal	2.1×10^3	3*	2.1	3*	460
GST124	Amorphous	110	2.8	2.3	–	–
	Distorted rock salt	1.1×10^3	3*	2.5	3*	42
	Hexagonal	1.3×10^3	3	2.2	3*	450

2. Experimental

Thin amorphous films of four compositions, GeTe, GeSbTe$_2$ (in the following denoted as GST112), GeSb$_2$Te$_4$ (GST124), and Ag$_{5.5}$In$_{6.5}$Sb$_{59}$Te$_{29}$ (AIST) were deposited by dynamic DC magnetron sputtering employing stoichiometric targets onto plane-parallel substrates made from undoped Si with dimensions about $10\times20\times0.55$ mm^3. The background pressure of the sputter system was on the order of 10^{-6} mbar, while typically an argon pressure of 5×10^{-3} mbar was established.

The PCM films were deposited only on a half of each substrate; the other half was masked and left uncovered. The thickness of the substrates was measured by means of a precision gauge with an error of ±1 μm; within this precision, the thickness of the substrates was found to be constant across the measured area. The thicknesses of the thin films d were measured within $\pm$ 10 nm using a surface profiler (Alpha-Step 500, Tencor); we obtained the following values: $d = 0.75$ μm for AIST, $d = 0.97$ μm for GST112, $d = 1.01$ μm for GST124, and $d = 1.12$ μm for GeTe.

The phase transition temperatures of the films were determined by means of differential scanning calorimetry (DSC), for which scratched-off pieces of equivalently sputtered films with total masses of 5–20 mg were heated at a constant heating rate of 1–50 K/min. The densities and crystal symmetry of all phases were determined by means of X-ray reflectivity. The density values obtained were subsequently used for calculating the changes in thickness of the films in the crystalline state. The resulting transition temperatures and densities are listed in Table 1.

A custom experimental setup for time-domain THz spectroscopy was used. A Ti:sapphire laser oscillator provided 810 nm, 80 fs pulses at a 76 MHz repetition rate. Linearly polarized THz pulses were produced by an interdigitated photoconducting emitter [13]. A weak part of the laser beam was directed on a 1 mm thick $\langle110\rangle$ ZnTe crystal for electro-optic sampling of the transmitted THz waves, yielding a useful spectral range of 0.25–2.5 THz. First, spectra of amorphous films were measured at room temperature in a simple mechanical holder. For measurements of crystalline phases, the samples were placed in a furnace with optical ports, using a clear aperture of 5 to 6 mm, and heated to the annealing temperatures given in Table 1. The whole THz beam including the furnace was enclosed in a rough vacuum chamber (at a pressure of about 20 mbar) in order to avoid water vapor absorption. A heating rate not exceeding 4 °C/min was used in order to reduce the in-plane stress and strain. After going through the phase transitions, the crystalline phases were annealed for 30 to 60 min before further data acquisition. As, during the heating, the furnace does not allow removal of the sample from the beam path in order to make reference measurements, these were performed right before the heating runs. The temperature dependence of the complex optical constants of silicon used as substrate material was acquired in an independent experiment.

3. Results and evaluation

The refractive index spectra of all samples were numerically calculated from the complex transmittance in the way described in detail in [12]. Since the optical thickness of the thin films is much lower than that of the substrates, it is important to ensure the highest possible precision in determining the thicknesses of film substrates, bare substrates, and thin films. Moreover, in the crystalline state of PCMs, the spectra of the real and imaginary parts of the refractive index $N(\omega)\equiv n+i\kappa$ have similar shapes and values; therefore, even a small error in n and/or in κ (typically ±1) will lead to a large offset of the real part $\varepsilon_1(\omega)$ of the permittivity $\hat{\varepsilon}\equiv N^2$. By contrast, the imaginary part $\varepsilon_2(\omega)$ and the related real part of conductivity $\sigma_1(\omega)$ can be determined with a lower relative error. A detailed discussion of the data treatment including errors in the calculated spectra can be found in [12]. For further data analysis, we converted the imaginary part of the permittivity according to the identity $\hat{\varepsilon}(\omega)\equiv i\hat{\sigma}/(\varepsilon_0\omega)$ to the real conductivity, $\sigma_1(\omega)=\varepsilon_0\omega\varepsilon_2(\omega)$, where ε_0 is the vacuum permittivity.

The spectra of the real parts of the permittivity and conductivity of the four materials in the amorphous phases are shown by symbols in Fig. 1. They contain no sharp features; the relative permittivity value amounts to several tens and tends to decrease towards higher frequencies. By contrast, the conductivity spectra tend to zero at low frequencies and display an increase with rising frequency.

These spectra can be described by a model based on a Lorentz harmonic oscillator:

$$\hat{\varepsilon}(\omega)\equiv\varepsilon_1+i\varepsilon_2=\varepsilon_\infty+\frac{f}{\omega_0^2-\omega^2-i\omega\Gamma} \tag{1}$$

where ε_∞ represents a high-frequency value of the permittivity (i.e. that in the middle infrared range) and ω_0 is the oscillator eigenfrequency; f and Γ denote its strength and damping, respectively. By means of fitting, we have determined parameters providing the best agreement of the model with the experimental data; the calculated curves are shown by solid lines in Fig. 1, and the resulting parameters are listed in Table 2 except for ε_∞ which, for the above-mentioned reasons, is subject to an error of the order of several tens and therefore has no physical meaning.

The experimentally obtained spectra of all samples in the crystalline phases are shown by symbols in Fig. 2. For the spectra of the real part of permittivity, note that, while their shapes are determined correctly, an unknown additive constant results from an experimental error, as mentioned above and explained