# GeSb thin films: read-write optical data storage on the subnanosecond time scale

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**Abstract:** The transition from the low reflectivity amorphous to the highly reflective crystalline phase of a-GeSb films is studied with fs time resolution. The results reveal an ultrafast transition to a new non-thermodynamic phase which is not c-GeSb as previously believed [1].



**OCIS codes:** (320.7130) Ultrafast processes in condensed matter, including semiconductors; (160.2750) Glass and other amorphous materials

There is currently considerable interest in laser induced phase transitions in Sb-rich GeSb thin films because of potential application of such films as media for optical data storage devices [2, 3, 4]. The key features which favor GeSb for this application are the large reflectivity difference between the amorphous and crystalline phase of GeSb (up to 20 % ) and the fact that it is possible to induce transitions back and forth between those phases in less than a nanosecond [4].

Apart from their importance for technological applications, these thin films also display scientifically intriguing phenomena. For example, Sokolowski-Tinten *et al.* reported an intriguing discovery in 1998: an ultrafast (200 fs) optically induced transition of amorphous GeSb to the crystalline phase [1].

In this paper we present a detailed experimental study of laser induced ultrafast phase transitions in GeSb alloys. We investigate the changes of the material by directly monitoring the full dielectric function over a broad energy range (1.7–3.5 eV) with 70 fs time resolution. This is achieved by measuring reflectivity spectra at various time delays after the optical excitation of the material at two distinct angles and subsequently

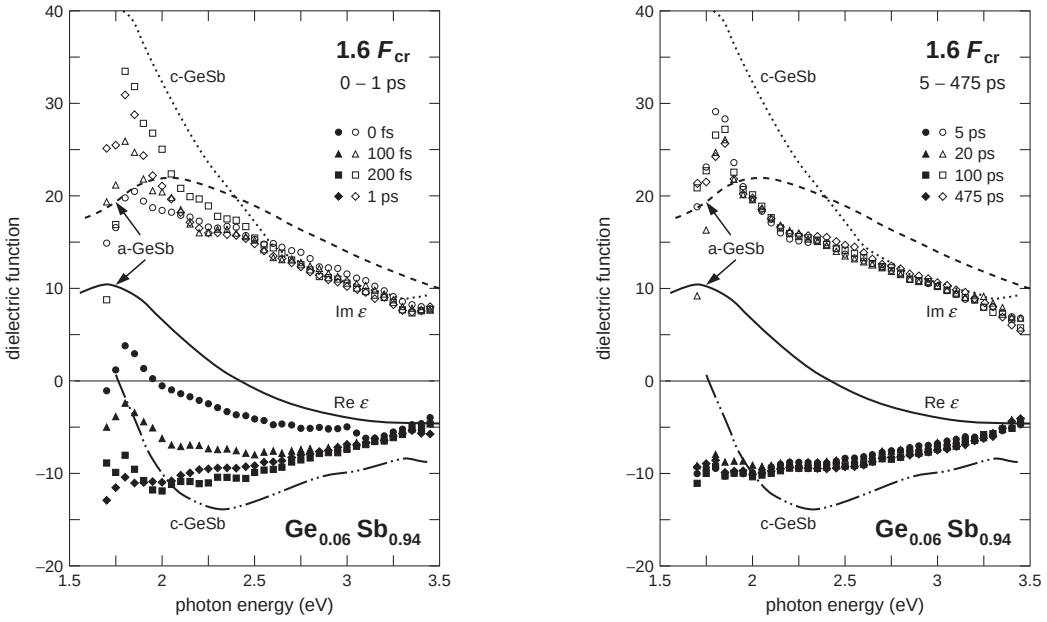


Fig. 1. Evolution of $\epsilon(\omega)$ from 0–475 ps for a pump fluence of 1.6 $F_{cr}$. The hollow symbols represent Im[$\epsilon(\omega)$] and the full ones Re[$\epsilon(\omega)$]. The dotted and dash-dotted lines show the imaginary and real part of the $\epsilon(\omega)$ of a-GeSb obtained by ellipsometry [6]; the dashed and full lines represent the corresponding values for c-GeSb according to our measurements of unpumped c-GeSb [6].

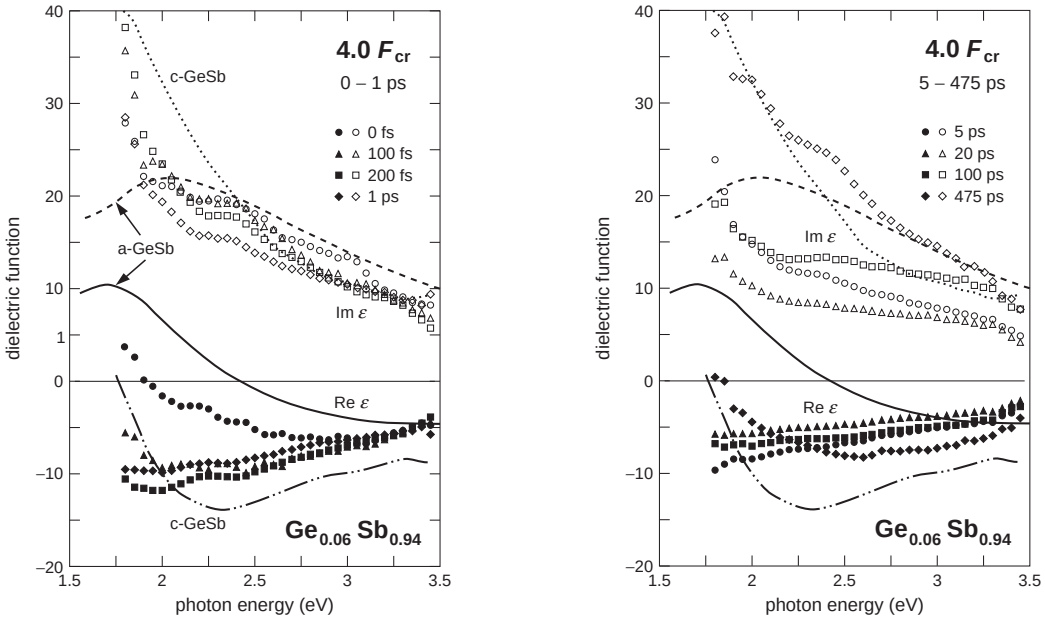


Fig. 2. Evolution of $\epsilon(\omega)$ from 0 – 475 ps for a pump fluence of 1.6 $F_{cr}$. The hollow symbols represent Im[$\epsilon(\omega)$] and the full ones Re[$\epsilon(\omega)$]. The dotted and dash-dotted lines show the imaginary and real part of the $\epsilon(\omega)$ of a-GeSb obtained by ellipsometry [6]; the dashed and full lines represent the corresponding values for c-GeSb according to our measurements of unpumped c-GeSb [6].

extracting the dielectric function at each time delay by inverting the Fresnel formulae. A more detailed description of the technique is given in Ref. [5]. We use an amplified Ti:sapphire laser system producing 50-fs pulses at 1-kHz repetition rate with pulse energies of up to 0.5 mJ. The sample was a 50nm film of originally amorphous $Ge_{0.06}Sb_{0.94}$ (hereafter denoted as GeSb) alloy deposited on a Glass substrate. At each angle the experiments were carried out in a standard pump probe geometry where the reflected portion of the white light probe is measured using a spectrograph.

To test the validity and accuracy of our technique we measured the reflectivity spectra of the unpumped material and compared the resulting dielectric function with previously obtained data from cw ellipsometry measurements of the same material [6]. The agreement achieved is excellent.

The dynamics of the material following excitation with the 50-fs pump pulse are strongly fluence dependent. We present here the results obtained at 1.6 and 4.0 times the threshold for crystallization, $F_{cr} = 0.22\,\mathrm{kJ/m^2}$.

Figure 1 shows the evolution of the dielectric function $\epsilon(\omega)$ from time zero to 475 ps after an excitation at 1.6 $F_{cr}$. The dielectric functions for both the amorphous GeSb and the crystalline GeSb are taken from unpumped measurements of the sample at fresh spots and previously irradiated (and thereby crystallized) spots respectively. The crystalline nature of the irradiated spots was demonstrated by TEM measurements elsewhere [4]. Both the real and imaginary part of $\epsilon(\omega)$ start drifting downwards immediately after excitation. Over the course of 200 fs the real part moves down until it reaches a level of around −10 across the entire frequency range. The imaginary part bends up slightly below 2.5 eV and begins to resemble the dielectric function of crystalline GeSb (c-GeSb). Both parts of $\epsilon(\omega)$ do not change significantly out to the end of the range of measured time delays (475 ps). Measurements at 1.2 and 4.0 times $F_{cr}$ show that this particular shape of $\epsilon(\omega)$ is fluence independent [6]. This fluence independence strongly suggests that the dielectric function represents a new phase which the material takes on within 200 fs. The dielectric function of this new phase is different of c-GeSb even though it closely resembles a Drude type dielectric function, suggesting the material takes on a metallic character. The exact nature of the phase can not be determined with the data at hand, but the new phase is likely to be either a liquid phase which is not in thermodynamic equilibrium or a solid disordered phase which is different from the original a-GeSb.

Figure 2 depicts the evolution of $\epsilon(\omega)$ for 4.0 $F_{cr}$. As for the excitation at 1.6 $F_{cr}$, the real and imaginary parts

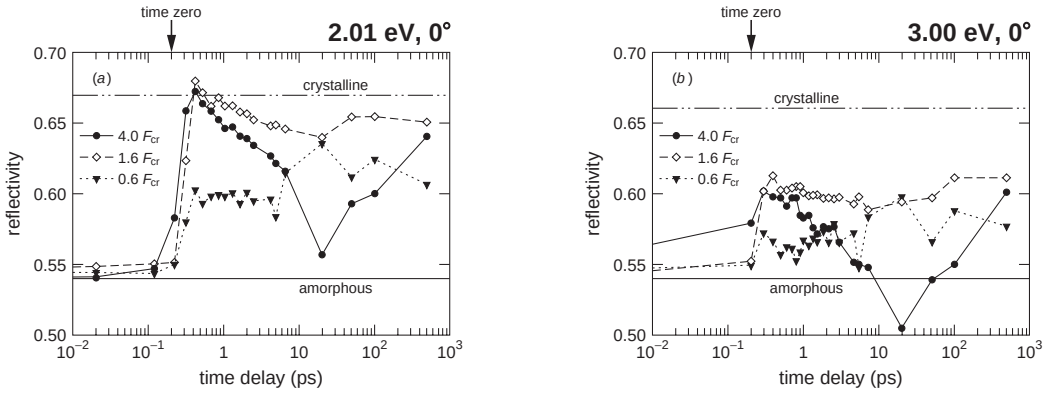


Fig. 3. Reflectivity transients for three different fluences for 0° angle of incidence at (a) 2.01 eV and (b) 3.00 eV.

of $\epsilon(\omega)$ start dropping immediately after excitation. The new phase appears earlier for this high excitation (after about 150 fs). More strikingly, the changes in the dielectric function are larger at long time delays. After reaching a low at 20 ps, the imaginary part starts rising, until at 475 ps, the low energy part lines up with the $\epsilon(\omega)$ for c-GeSb and the high energy part with the $\epsilon(\omega)$ for a-GeSb. The real part also starts bending down at 475 ps approaching the real part of c-GeSb. So, after about 0.5 ns, the dielectric function starts approaching that of c-GeSb. This observation is indicative of an unusually fast crystallization process, in agreement with earlier picosecond measurements of the single angle reflectivity at two wavelength. [7].

As mentioned before, Sokolowski-Tinten and co-workers reported an ultrafast phase transition from a-GeSb to c-GeSb based on reflectivity measurements at a single energy of 2 eV and at a single angle of 0° [1]. Under these specific conditions the reflectivity values at 200 fs closely match those of the crystalline phase. Figure 3 shows the evolution of the reflectivity at 2.01 eV and 0° as calculated from the dielectric function values we report here. The data in Figure 3 (a) are in excellent agreement with those of Ref. [1]. Indeed, after only 200 fs the reflectivity takes on the same value as that of c-GeSb, even though the dielectric function is different. Our measurements thus show that the previously reported match in reflectivity values between that of the new phase and c-GeSb is a coincidence. At any other frequencies or angles, the reflectivity does not approach that of c-GeSb (see, *e.g.*, Figure 3 (b), which shows the reflectivity transients at 3.0 eV and 0°).

In conclusion, we observe an ultrafast change of a-GeSb into a new non-thermodynamic phase after excitation with a fs laser pulse. The phase does not correspond to c-GeSb as stated in previous work. Future experimental studies or theoretical modeling should be able to illuminate on the exact nature of the observed new phase. Furthermore we observe first signs of laser induced crystallization after only 500 ps which makes GeSb thin films very attractive for rapid read-write optical data storage applications.

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