

Ultrafast Phase Transition Dynamics in GeSb Alloys

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Abstract: We measure the femtosecond time resolved dielectric function of a-GeSb after excitation with an ultrashort laser pulse. The results reveal an ultrafast transition to a new non-thermodynamic phase which is not c-GeSb as previously believed [1].

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There has been considerable research effort on laser induced phase transitions in Sb-rich alloys since the 1980s [2, 3, 4]. Interest in these materials was triggered by the possibility to use them as media for optical data storage devices. The key features which favoured especially 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 from one phase to the other and back on very short time scales [4].

Apart from their importance for technological applications, these alloys also display scientifically intriguing phenomena. Sokolowski-Tinten et al reported perhaps the most fascinating discovery in 1998: an ultrafast (200 fs) transition of amorphous GeSb to the crystalline phase [1].

In this paper we present the most thorough experimental study to date 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 eV - 3.5 eV) with 100 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 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 used an amplified Ti:sapphire laser system

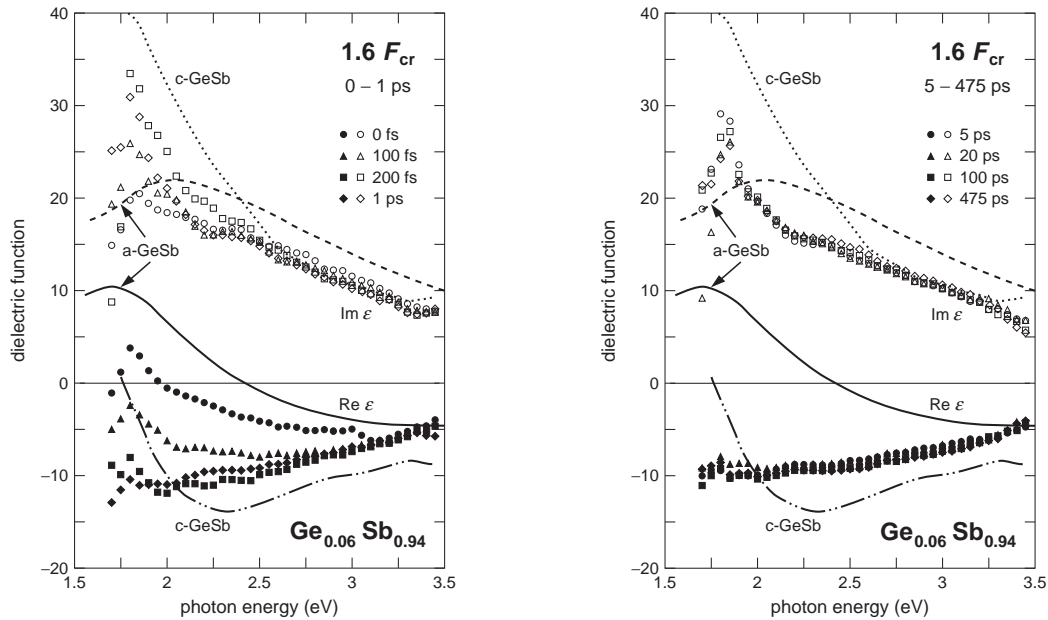


Fig. 1. Evolution of $\epsilon(\omega)$ from 0 - 475 ps for a pump fluence of $1.6 F_{cr}$. The hollow symbols represent $\text{Im}[\epsilon(\omega)]$ and the full ones $\text{Re}[\epsilon(\omega)]$. The dotted and dash-dotted lines show the imaginary and real part of the $\epsilon(\omega)$ of a-GeSb 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].

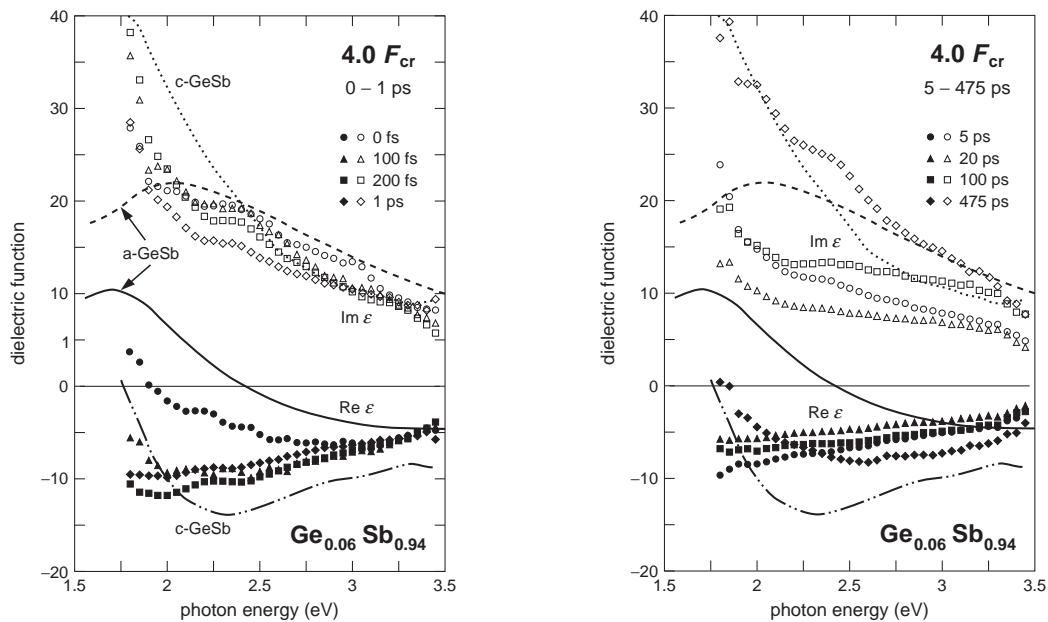


Fig. 2. Evolution of $\epsilon(\omega)$ from 0 - 475 ps for a pump fluence of $1.6 F_{cr}$. The hollow symbols represent $\text{Im}[\epsilon(\omega)]$ and the full ones $\text{Re}[\epsilon(\omega)]$. The dotted and dash-dotted lines show the imaginary and real part of the $\epsilon(\omega)$ of a-GeSb 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].

producing 50-fs pulses at 1-kHz repetition rate with pulse energies of up to 0.5 mJ. The sample was a 50 nm film of originally amorphous $\text{Ge}_{0.06}\text{Sb}_{0.94}$ (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 was measured using a spectrograph.

To test the validity and accuracy of our technique we measure the reflectivity spectra of the unpumped material and compare 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 which we determined to be $F_{cr} = 0.22 \text{ kJ/m}^2$.

Figure 1 shows the evolution of the dielectric function $\epsilon(\omega)$ from time zero out 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 proven 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 reaches a form that resembles the shape of the crystalline GeSb (c-GeSb) but is still clearly distinct from it. Both parts of $\epsilon(\omega)$ do not change significantly out to the end of the range of measured time delays (475 ps). This particular shape of $\epsilon(\omega)$ turns out to be fluence independent as other measurements at 1.2 and 4.0 times F_{cr} show [6]. This fact strongly suggests that it represents a new phase which the material takes on within 200 fs. Even though it clearly displays metallic character in that it closely resembles a Drude type $\epsilon(\omega)$ it certainly is not the same phase as c-GeSb. The exact nature of the phase can not be determined with the data at hand, but it is very likely that it is either a liquid phase which is not in thermodynamic equilibrium or a solid disordered phase which is different from the a-GeSb of the fresh material.

Figure 2 depicts the evolution of $\epsilon(\omega)$ for $4.0 F_{cr}$. Very similarly to the excitation at $1.6 F_{cr}$, the real and imaginary parts of $\epsilon(\omega)$ start dropping immediately after excitation. As expected the new phase which was

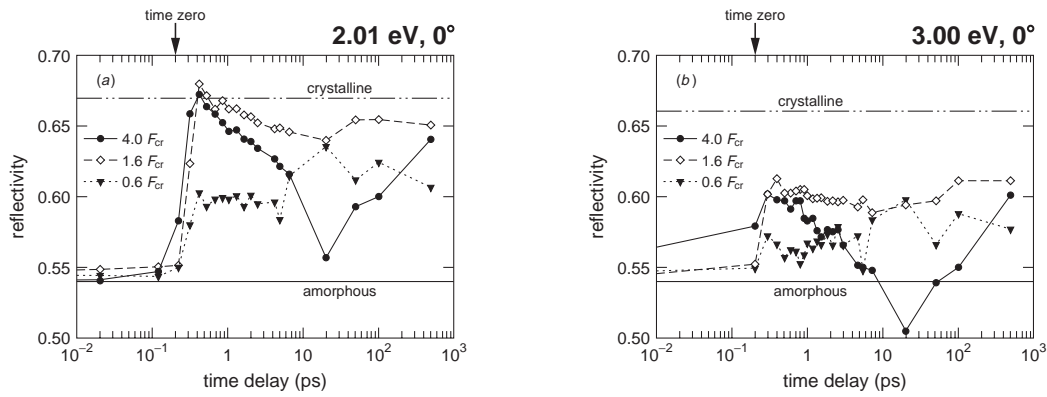


Fig. 3. Reflectivity transients for three different fluences for 0° angle of incidence at 2.0 eV (left hand side) and 3.0 eV (right hand side).

observed at the lower fluence excitation appears a little earlier for this high excitation (after about 150 fs). More strikingly, there is significant dynamic of $\epsilon(\omega)$ at longer time delays. After reaching a low at 20 ps, the imaginary part starts rising until it reaches a striking shape at 475 ps, where 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 overall the $\epsilon(\omega)$ after about 0.5 ns starts approaching that of c-GeSb. This strikingly similar shape is indicative of an unusually fast crystallization process. Crystallization within 400 ps in GeSb alloys has been observed before [7].

As mentioned before, Sokolowski-Tinten and co-workers observed an ultrafast phase transition from a-GeSb to c-GeSb [1]. That reflectivity experiment was carried out at a single energy of 2 eV and at a single angle of 0° . It turns out that at these very specific parameters the reflectivity time transients in fact do suggest very convincingly that the material reaches the crystalline phase after 200 fs.

Figure 3 shows the reflectivity transients for exactly the abovementioned parameters as calculated from the dielectric function values using the Fresnel formula. Plot (a) is in excellent agreement with Figure 2 of Ref. [1] indicating that both experiments yield compatible results. The reflectivity reaches the exact value of c-GeSb after only 200 fs. However, this fact is only a coincidence for these very special parameters as the dielectric function values show. Choosing any other set of parameters results in very different reflectivity transients. In Figure 3 (b) we plot the reflectivity transients for 3.0 eV and 0° which, as expected, do not hint towards the appearance of c-GeSb at all.

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. Further experimental studies or theoretical modelling should be able to illuminate on the exact nature of the observed new phase.

References

1. Sokolowski-Tinten, K., Solís, J., Bialkowski, J., Siegel, J., Afonso, C. N. and von der Linde, D. (1998), Phys. Rev. Lett. **81**, 3679.
2. Gravelstein, D.J. (1988) Appl. Opt. **27**, 736.
3. Suzuki, M., Furuya, K., Nishimura, K., Mori, K. and Morimoto, I. (1990) Proc. SPIE **1316**, 374.
4. Afonso, C. N., Solís and Catalina, F. (1992) Appl. Phys. Lett. **75**, 7788.
5. Huang, L., Callan, J. P., Glezer, E. N. and Mazur, E. (1998), Phys. Rev. Lett. **80**, 185 and references therein.
6. A more detailed paper including other data is going to be published elsewhere.
7. Siegel, J., Afonso, C. N., Solís, J. (1999), Appl. Phys. Lett. **75**, 3102.