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Phase-change optical recording: the role of confinement

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A new insight into the amorphous nature of the recorded bits in optical phase-change recording. Pressures up to 5-6 GPa are expected upon melting of a confined bit while we cannot concluded that drives the bits into the amorphous state, the results shown in this paper clearly demonstrate that pressure is an important factor for the amorphization process in a device structure and should be considered on the way for improvement of current and development of novel optical discs and electrical phase-change memories for future uses.

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One of the major industrial applications of chalcogenide glasses is in phase-change data storage devices [1]. The latest industrial implementation of such a device is the digital versatile disc (DVD) that appeared on the market in the mid 1990s. The idea of phase change-recording dates back to the mid 1960s when S.R. Ovshinsky first suggested to use differences in the electrical and optical properties between the amorphous and crystalline phases of Te-based chalcogenides for data storage [2].

The idea of phase-change recording is quite simple. When a melt is cooled down slowly, such that the structure always remains in thermal equilibrium, upon reaching the crystallization temperature the material crystallizes, i.e. is transformed into a solid state with a well-defined periodic structure. If, on the other hand, the cooling rate is fast, then at a certain temperature the viscosity of the liquid increases to such an extent that the structure can no longer relax to follow the changes in temperature; one obtains a supercooled liquid and then a glass. Different from the crystallization temperature, the glass-transition temperature can only be defined over a range of temperatures; the temperature of a glass transition depends on the cooling rate.

Once in the solid state, the glass, if kept at a temperature close to the glass transition temperature, crystalllizes. On the other hand, rapid heating of the crystalline material to a temperature above the melting point and subsequent rapid cooling (quenching) can produce a glassy state. This process is envisaged in the glass-formation diagramme shown in Fig. 1.

The material can also be heated by light. Exposure of an amorphous material to laser light of such intensity that it is heated above the glass-transition temperature results in its crystallization while short and intense laser pulses melt the material and - provided the heat dissipation rate is fast enough - an amorphous recorded bit is formed.

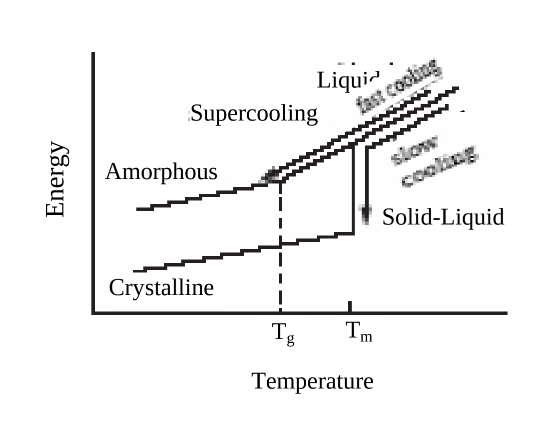

Fig. 1. Glass-formation diagramme.

The most used materials for commercial discs include $Ge_2Sb_2Te_5$ (GST) used for DVD-RAM and Ag-In-Sb-Te (AIST) alloys for DVD-RW [1]. Interestingly, the same materials give rise to the best performance of the so-called super-resolution near-field structure (Super-RENS) discs that allow the reading of bits beyond the diffraction limit, although the readout mechanism is believed to be different from conventional phase-change memory [3]. Furthermore, the same materials are used in Ovonic unified memory (OUM) [2] and very recently for cognitive computing [4]. It has even been argued [5,6] that phase-change memory is likely to replace the presently wide-spread flash memory due to its scalability and potentially unlimited rewrite capabilities. The great importance of phase-change chalcogenide alloys for advanced memory applications clearly requires a much deeper understanding of the underlying materials properties than currently exists.

When a crystalline material is heated (and melted) its volume increases due to (i) thermal expansion and (ii) subsequent transformation into a less dense disordered state. In devices, the recorded bits are confined. As a result, the volume of the recorded bit cannot expand and experiences rather strong compressive forces. A simple estimate based on the values of the thermal expansion coefficient [7], density change upon disordering [8], and the bulk moduli [9] yields an impressive value of 5-6 GPa.

Since pressure is a important thermodynamical parameter it can be surmised to have a strong effect on phase stability. It has long been known that similar (biaxial) strains in semiconductors can stabilize metastable phases and ordering [10]. However, up to now, only the role of temperature has been considered in the phase diagram, which is rather unusual in the framework of thermodynamic descriptions and it is only very recently that we have undertook a study of pressure effect on phase-change materials [9].

In the initial work we used a $Ge_2Sb_2Te_5$ composition. Samples were prepared by the rf-sputtering of a $Ge_2Sb_2Te_5$ target [11] and were subsequently annealed at 180 °C for 2 hours in an Ar atmosphere to induce crystallization. For X-ray diffraction measurements (λ=0.71073 Å) the annealed film was scraped off the substrate and mixed with NaCl that acted as a pressure marker; a 4:1 methanol:ethanol mixture was used as a pressure transmitting medium. Angle-dispersive x-ray diffraction (XRD) data at high pressures were measured using a diamond anvil cell. More details can be found elsewhere [12].

The stable GST structure is trigonal [13]. At the same time, XRD experiments on thin layers have indicated that they crystallize into a higher-symmetry metastable structure that is similar to the rocksalt structure with Te atoms forming one face-centered cubic (fcc) sublattice and Ge and Sb species occupying sites on the other fcc sublattice with 20% of the sites in the latter vacant [14]. In this work, we deal with the metastable crystal (cubic) structure that is relevant to phase-change memories. While the local structure of metastable $Ge_2Sb_2Te_5$ is distorted with Ge and Sb atoms displaced from the center of the cell [11,15,16], long-range order is best described as having the rocksalt structure with a large thermal factor and in what follows we use pseudo-cubic peak indexing.

Fig. 2 shows the pressure-induced evolution of the observed XRD pattern. One can see that in the pressure range 0 to 10 GPa, compression results in a simple shift of all peaks to larger angles indicating a decrease in the unit cell under compression. The bulk moduli K_0 and K' obtained by fitting the Birch-Murnaghan equation of state (EOS) [17] to the experimental data (Fig. 1b) are K_0 = 41±2 GPa and K' = 3.8±0.6; these values are rather close to the corresponding values for GeTe (K_0=49.9 GPa, K'=3.76 [18]).

At higher pressures, the intensity of the GST peaks decreases and the peaks broaden: a behaviour indicative of amorphization. At pressures above 20 GPa, the sharp crystalline peaks are essentially replaced by a broad band although a small remnant of the crystalline 220 peak is still visible.

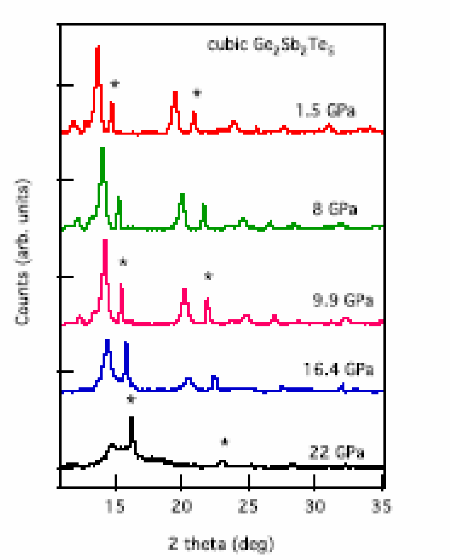

*Fig. 2. Pressure-induced changes of the XRD pattern of GST upon compression. The peaks marked by * are the corresponding peaks of the NaCl marker. The pressures are shown at the right side of each plot.*

The observed amorphization is rather atypical. It can, for example, be noted that GeTe does not amorphise upon compression. Although pressure-induced amorphization has been reported for numerous materials [19], it typically happens in corner-linked polyhedral compounds, hydrogen bonded materials and van-der-Waals solids. When a material with the compact rocksalt structure (both ionically and/or covalently bonded) is subject to pressure it usually transforms to a CsCl-type structure [20] since the latter possesses an increased packing density.

The observed pressure-induced amorphization is irreversible, i.e. the initial “cubic” structure is not restored upon decompression.

To explain this rather unusual behaviour of GST in comparison with the more typical case of a NaCl to CsCl type transformation several suggestions were made [9], based on differences between GeTe and $Ge_2Sb_2Te_5$ structures.

First, it was noted that the presence of larger Sb atoms on the same crystallographic sites as Ge is likely to generate inhomogeneous stresses that may drive the system into the amorphous state through the phase decomposition into Ge-Te and Sb-Te phases. Amorphization via nanophase separation is often a driving force for pressure-induced amorphization in cases when the total volume of the decomposed phases is smaller than the volume of the starting material. It should be noted that the nanophase separation into Ge-Te and Sb-Te phases was previously suggested to take place during photo-induced amorphization [21] An important issue may be that the compositions that actually do work in devices are always quasibinary GeTe-Sb_2Te_3 alloys which suggest a possibility of existence of different phases.

Another major difference in the structure is presence of vacancies in the metastable cubic $Ge_2Sb_2Te_5$ phase. The amorphization can thus occur through squeezing out of vacancies with subsequent disordering of the structure. Absence of pressure-induced amorphization in the stable trigonal $Ge_2Sb_2Te_5$ phase that contains no vacancies provides grounds for this possibility.

Our results offer a new insight into the amorphous nature of the recorded bits in optical phase-change recording. As already mentioned, pressures up to 5-6 GPa are expected upon melting of a confined bit. While we cannot conclude based on the present results alone that the generated pressure is the major force that drives the bits into the amorphous state, the presented results clearly demonstrate that pressure is an important factor for the amorphisation process in a device structure and should be considered on the way for improvement of current and development of novel optical discs and electrical phase-change memories for future uses. The above discussion is also applicable to OUM and other types of phase-change memories when (whatever the inducing stimuli) a recorded amorphous bit is confined within a crystalline medium or vice versa.

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