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Report:

Introduction

Phase Change Materials (PCMs) have the property to reversibly switch, through controlled (local) heating, between an amorphous and a crystalline phase. These two phases exhibit a large contrast both in electrical and optical properties. This makes PCMs very interesting for storing information. Indeed, they have been used for a long time in ReWritable Compact Disks (where writing is performed by laser heating and reading by low power laser optical reflectivity measurement). More recently it has been realized that writing and reading can be performed using an electrical current, and thus opening the path to Phase Change Random Access Memories (PCRAM). They constitute a very promising alternative to Flash technology, which is reaching fundamental limits. One of their key advantages is their speed (in the 10's of ns), their scalability, and intrinsic compatibility with embedded memories processes. One of the most studied PCM is Ge2Sb2Te5 (commonly named GST in the literature), which has a crystallization temperature close to 150–170 °C. This temperature is too low for long-enough data retention in many applications (e.g. automotive). To address this issue, compositionally optimized Ge-rich GST (GGST) has been developed by STMicroelectronics [1] having a crystallization temperature of about 350°C. *In-situ* X-ray diffraction experiments performed at low heating rates (2°C/minute) reveal a two-phases crystallization process [2] in this material where Ge crystallization/segregation precedes the one of GST. Although these experiments do bring a wealth of interesting information on the crystallization mechanism in this material, they are performed in conditions which are far from real memory cells operating conditions: (i) they are performed at heating rates of few K/s that are extremely far from those occurring in real devices (typically 10^{10} K/s). It is quite reasonable to believe that phenomena may be vastly different with so many orders of magnitude difference; (ii) furnace heating allows crystallizing the as-deposited amorphous material but does not allow re-amorphising the crystal by quenching from the liquid state.

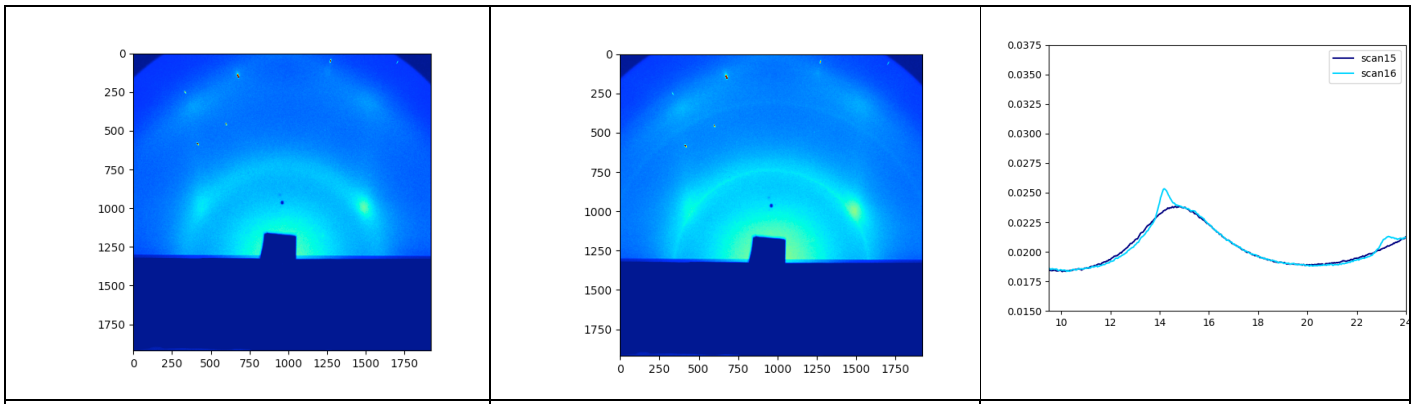
It appears thus highly desirable to perform time-resolved experiments while cycling the material through the crystallized (c) and amorphous (a) states at time scales akin to what happens in real devices (ns-µs typically). Although phase switching is performed via Joule-heating in memory devices, laser switching is an ideal alternative for in situ time-resolved experiments considering the easier realization of actual pump-probe measurements.

Samples

Thin film stacks with the following structure: 15 nm SiN/50 nm GGST/15 nm SiN have been deposited on 300 mm diameter Si (001) substrates by sputtering at ST Crolles clean room facility. Here SiN stands for amorphous silicon nitride, which acts as a capping layer preventing the chalcogenide mixture to be oxidized. The large amount of available material (300 mm wafer) allows testing many different experimental conditions and – in some cases – using a shoot-and-move approach. 5 cm long and 1 cm wide samples have been mounted on the goniometer head.

Description of the experiment at the beamline: methodology and results

In order to maximise the scattered intensity on the 2D rayonix detector an incidence angle of 1° and the pink beam from undulator (E=15.4 keV) were chosen. Considering an X-ray beamsize of 24µm (V)*49µm (H) this translates in a beam footprint of 1.37 mm*49 µm on the sample. A typical image of the scattered signal (energy 15.5 keV) from a pristine sample is shown in figure 1(a). Broad humps from amorphous layers are evidenced together with more intense features arising from Si single crystal TDS (Thermal Diffuse Scattering). A 800 nm (Ti-Sapphire) 100 ps laser beam with a size of 4 mm along x (X-ray beam direction) and 190 µm along y. A Pockels cell was used for controlling the frequency of laser pulses in gated mode and the in-plane rotation of a quarter plate was used for varying the laser fluence between 35 mJ.cm^{-2} (10°) and 220 mJ.cm^{-2} (45°).
As shown in figures 1(b) and 1(c) crystallization has been observed under proper laser illumination conditions.



a b c

Figure 1: Detector images (0.5 s counting time). (a) Pristine state and (b) after 5000 laser shots (197 mJ/cm^2). (c) Comparison of radial scans (abscissa is two theta in degrees) show the appearance of Ge **111** and Ge **220** peaks evidencing that part of the material has crystallized.

A systematic investigation of the influence of laser fluence and number of shots has been undertaken. Figure 2 is a qualitative representation of the crystallized phases observed as a function of laser fluence and number of laser shots. Interestingly there are several areas in this "phase diagram" where only one crystallized phase is observed. This is in striking contrast with what happens during furnace anneals.

	12	29	54	84	117	146	170	185	189	energy (mW)
	14	34	63	98	136	170	197	215	219	fluence (mJ/cm2/shot)
50										
100										
250									GST	
500			Ge	Ge					GST	
750			Ge	Ge				GST	GST	
1000		Ge	Ge	Ge	Ge	Ge	GST / Ge	GST	GST	
2500		Ge	Ge	Ge	Ge	Ge / GST	GST / Ge	GST / Ge	GST / Ge	
5000		Ge	Ge	Ge	Ge / GST	Ge / GST	GST / Ge	GST / Ge	GST / Ge	
10000		Ge	Ge	Ge	Ge / GST	GST / Ge	GST / Ge	GST / Ge	GST / Ge	
nb. shots										

Figure 2: Qualitative diagram of observed crystalline phases as a function of the number of laser shots (vertical) and laser fluence (horizontal.

More quantitatively we have fitted signals such as the one shown in figure 1.c with a double Gaussian (Ge **111** diffraction peak and amorphous hump). The results are shown in figure 3 where the evolution of peak integrated intensities, position and integral breadths are plotted as a function of the number of laser pulses for a laser fluence of 35 mJ.cm^{-2}. Several interesting features are worth noting: (i) the integrated intensity of Ge **111**, which is related to the volume of crystallized

Ge, shows a monotonous increase when the number of pulses increases above 2000; (ii) the integral breadth is initially decreasing fast, which indicates probably an increase in crystal size from 20 to 60 Å and then decreases much more slowly above about 2000 laser pulses; (iii) the Ge **111** peak position shows a 1.5% decrease until 2000 pulses which corresponds to a lattice expansion of the same amount and then reaches the value expected for bulk Ge. Meanwhile the amorphous hump shows an evolution above 2000 pulses characterized by a slow decrease in integrated intensity, a decrease in integral breadth and a shift towards smaller q-values. It is worth emphasizing that these preliminary results indicate the formation via laser irradiation of extremely small Ge crystallites (to be confirmed by electron microscopy), which may present interesting electronic properties especially in the regime below 2000 pulses.

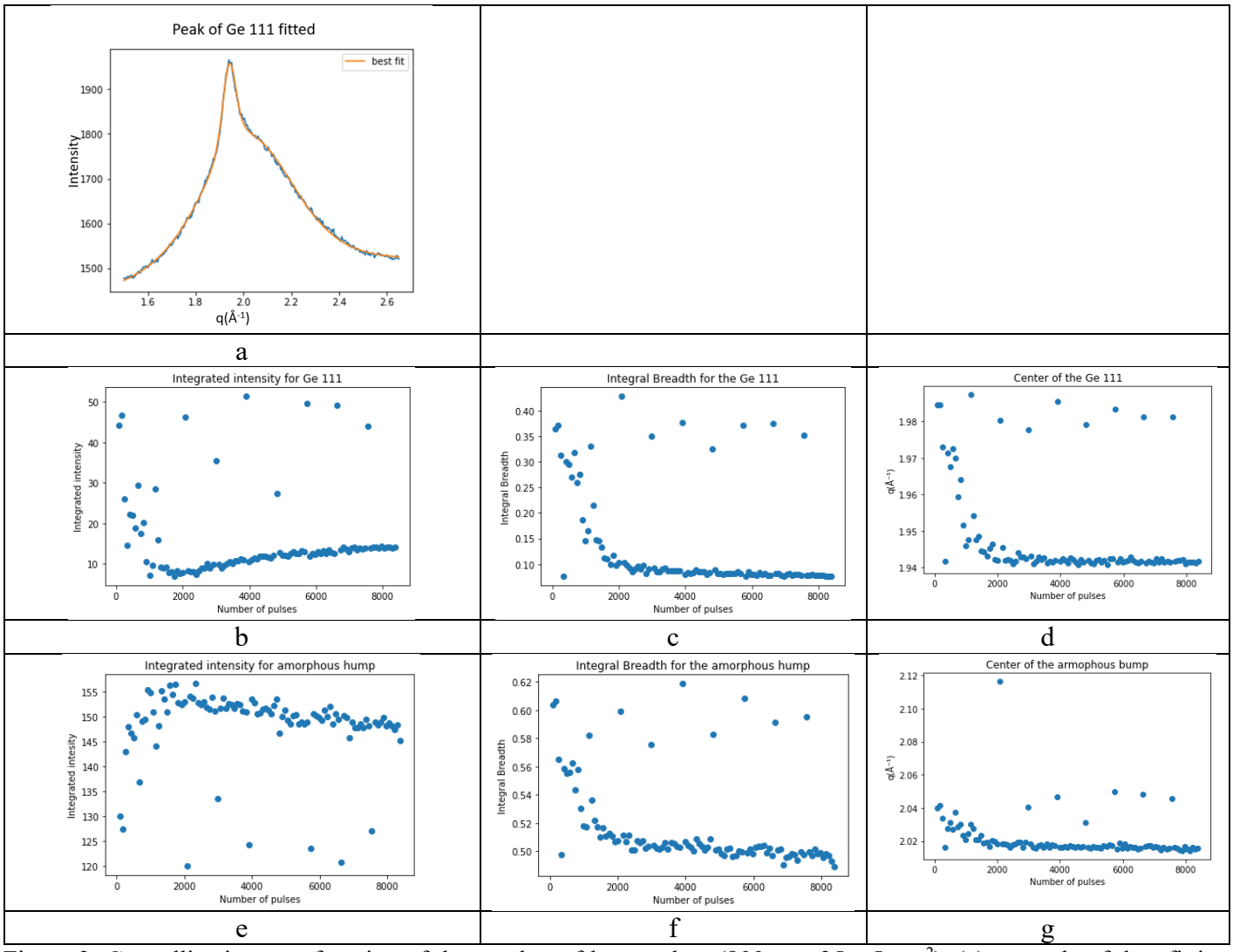


Figure 3: Crystallization as a function of the number of laser pulses (800 nm, 35 mJ.cm^{-2}). (a) example of data fitting with a double Gaussian. The narrow peak at 1.92 Å^{-1} is Ge **111**. Integrated intensity (b and e), integral breadth (c and f), and peak position (d and g), respectively for Ge **111** and amorphous hump.

Work is in progress to analyse the full range of investigated fluences, which includes GST phase and coexisting Ge and GST phases (see figure 2).

It is worth noting that it was not possible, in the investigated range of laser parameters, to induce amorphization of the crystalline phases. This would probably need another laser setup such as the Nd:YAG laser available at ID09. We have asked for a new beamtime for investigating amorphization using this laser since time was not sufficient to change the laser setup in the present experiment.

Based on this investigation of crystallization of GGST under the laser beam we have undertaken detailed stroboscopic pump-probe experiments aimed at looking at the fast dynamics of these GGST samples. Since the samples crystallize even at the lowest laser fluence both pump-probe at single location and pump-probe at varying locations have been performed. Figure 4 shows a time resolved experiment performed at a laser fluence of 35 mJ.cm^{-2}. A strong reversible signal at the Ge **111** position (1.92 Å^{-1}) is evidenced through the difference signal and is maximum for a time delay of 600 ps. Its relaxation is exponential with a characteristic time of 13 ns. A detailed analysis (through peak fitting and also thermal modeling) of this pump-probe experiment is underway. We hypothesize that this signal originates from the transient thermal response of Ge nano-crystals that are not detectable on the raw diffraction pattern.

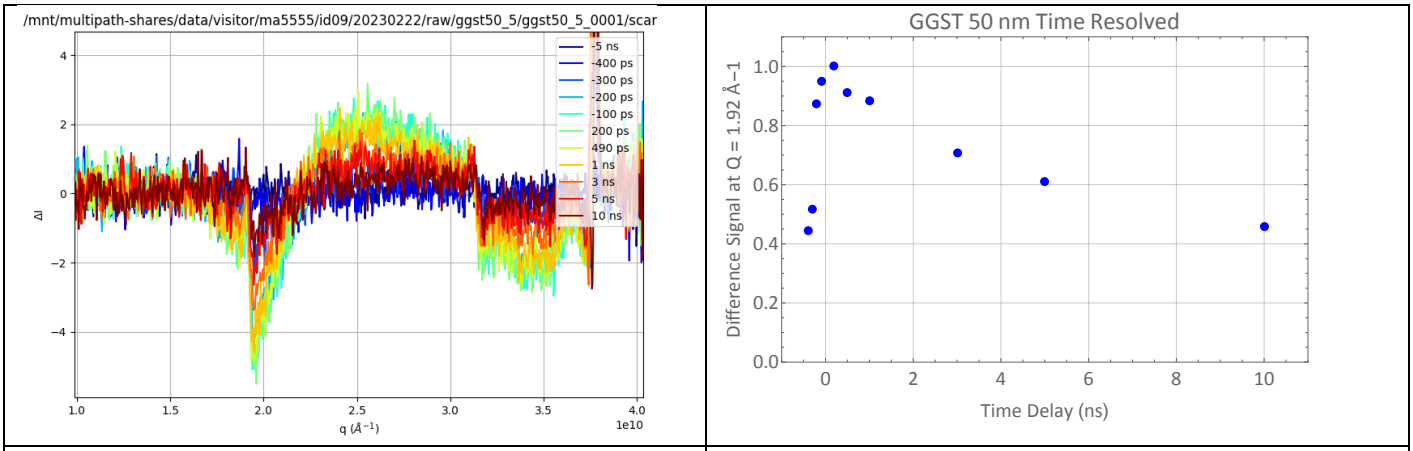


Figure 4 : (a) Time-resolved experiments performed in strobsoscopic pump-probe mode (800 nm, 35 mJ.cm^{-2}). Time zero (synchronization between laser pump and X-ray probe) is around-400 ps. The figure exhibits the different difference-response signals between delayed and non-delayed excitations for time delays between 0 and 10.4 ns. (b) Evolution of difference peak at 1.92 Å^{-1} (Ge **111**) vs time delay.

Conclusions and future work

This was a very successful beamtime. For the first time laser-induced crystallization of Ge-rich Ge-Sb-Te (GGST) 50 nm films has been observed. It is being quantified in a very systematic way and – coupled with thermal simulations – will yield invaluable results on the fast crystallization process in GGST. This is essential information for the understanding of embedded memory cells produced by STMicrolectronics.
We have been able to find the conditions for crystallization of 50 nm thin films (fluence, number of pulses with 100 ps - 800 nm laser beam (best compromise between available energy per pulse and time resolution). Interestingly it seems different laser fluences and/or number of laser pulses may promote selectively crystallization of Ge or GST. We have also evidenced a very interesting transient effect at the few 100 ps time scale that may be attributed to the thermal response of Ge nanocrystals embedded in the Ge matrix. These Ge nanocrystals might be the signature of the very early stages of crystallization, undetected by other means.

These first successful experiments still need being analysed in more detail but they clearly offer the possibility to investigate the very early stages of crystallization of GGST and the dynamics of Ge nanocrystals embedded in the amorphous matrix. These dynamics is probably highly dependent on the actual viscous and thermal properties of the amorphous medium. The amorphous phase that results from vapor condensation, having probably different physical properties than the one obtained by freezing the liquid, it appears thus highly desirable to perform similar time-resolved experiments while cycling the material through the crystallized (c) and amorphous (a) states. This is the topic of the proposal that has been submitted on March 1st 2023, immediately after the present experiment.

References

[1] P. Zuliani et al., IEEE Trans Electron Devices 60, 4020 (2013).
[2] O. Thomas *et al*., Microelectronic Engineering 244, 11573 (2021).