Comparison of data retention measured by static laser testing and in PCRAM devices

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ABSTRACT

Phase change materials are often evaluated for their thermal stability properties by measuring crystallization temperatures as function of heating rate or during isothermal annealing processes using, for example, resistivity versus temperature measurements, differential scanning calorimetry or time-resolved x-ray diffraction. These measurements are typically performed on as-deposited films. We have developed a method to measure data retention for amorphous, melt-quenched materials using a static laser tester combined with isothermal annealing in a furnace. The results show a much better data retention for as-deposited amorphous films compared to melt-quenched amorphous material. It has been known that as-deposited amorphous films can have much longer crystallization times compared to melt-quenched amorphous material. This was attributed to the fact that in the latter case no nucleation is required because the melt-quenched material typically is surrounded by crystalline material. In addition, the melt-quenched material might contain tiny crystallites that will accelerate crystallization. We find that the data retention results on as-deposited, amorphous films greatly overestimate the performance of the same phase change material in actual phase change random access memory (PCRAM) devices. Laser testing on melt-quenched material leads to a better prediction of the performance of a given phase change material in PCRAM devices.

Key words: data retention, laser testing, melt-quenched phase change material

1. INTRODUCTION

Data retention is one of the most important properties when a new phase change materials is considered for Phase Change Random Access Memory (PCRAM) technology. The most reliable results for data retention of a new phase change material are obtained by fabricating PCRAM cells and measuring the data retention as function of temperature, for various RESET conditions, and after various cycle numbers. However, since PCRAM device fabrication using CMOS technology can take several months the turn-around time for results on a new material is relatively long. On the other hand it is possible to measure crystallization temperatures and retention of the amorphous phase simply on as-deposited amorphous films. This has been done by various methods including resistivity versus temperature measurements, differential scanning calorimetry, time-resolved x-ray diffraction, static laser testing, or combinations of these methods [1-5]. Either heating ramps at different ramp rates or isothermal annealing experiments can be performed to evaluate the stability of the amorphous phase and estimate an activation energy for crystallization.

Typically, the melt-quenched amorphous material in PCRAM devices in the RESET state crystallizes at lower temperatures than measurements on as-deposited films would predict [6]. In addition, the crystallization temperature for devices also depends on the actual RESET conditions, for example a high voltage RESET pulse leads to a higher

crystallization temperature than a slightly lower voltage RESET pulse [6]. This confirms that as-deposited, amorphous and melt-quenched, amorphous materials can have different crystallization properties which was also evident in static laser testing experiments [7]. This can be attributed to the fact that melt-quenched material typically has an interface to a crystalline region, so that nucleation is not required for crystallization, and often the melt-quenched material contains very small crystallites that enable easy crystallization [8]. It is even possible that the crystal growth itself in the amorphous as-deposited state is slower than in the melt-quenched state [9].

In this work we use a static laser tester to produce melt-quenched amorphous areas in crystalline films and measure the data retention of these melt-quenched areas by annealing in a furnace to different temperatures and measuring reflectance after annealing. We compare data retention results obtained from such laser testing with data retention results from as-deposited amorphous films and PCRAM cells with the same phase change material. We show that laser testing of melt-quenched material is a better method to predict material performance in PCRAM devices than measurements of crystallization behavior of as-deposited materials.

2. EXPERIMENTS

Thin films of the phase change material Ge-Sb-Te were deposited by sputter deposition from a compound target. The film composition was selected to be Sb rich compared to $Ge_2Sb_2Te_5$ in order to quickly verify the consistency between laser testing and device thermal testing. Materials with better data retention, suitable for product use, would take much longer time (or much higher temperature) to verify the laser process as a viable means to study phase change materials. Sb-rich materials are also of interests for applications where switching speed is of great importance compared to data retention, e.g. DRAM replacement. The film composition was measured by a combination of Rutherford Backscattering Spectrometry (RBS) and Particle Induced X-ray Emission (PIXE) and was 23.3 ± 0.5 at. % Ge, 27.3 ± 5 at. % Sb and 49.4 ± 5 at. % Te. For laser testing 50 nm thin films of Ge-Sb-Te were deposited on 30 nm SiO_2 on Si substrates. The thin oxide film acts as a heat barrier and allows to reach the melting point in the phase change thin film with the available laser power, but also enables fast enough quenching of the material into the amorphous solid phase during cooling.

The laser tester includes a 160mW diode laser with a peak wavelength at 658 nm. This is pulsed with varying amplitude and duration to affect heating of the phase-change sample. A separate highly attenuated HeNe continuous wave laser at 633 nm is used to probe the sample's optical reflectance before and after heating. The two laser beams are first simultaneously introduced into a single mode optical fiber so as to filter out higher order laser modes, especially from the HeNe laser, and so precisely align and shape the two beams along the same optical path. The two are then simultaneously passed through a polarizing beam splitter cube and a Faraday rotator which rotates the polarity 45 degrees. The beams are then passed through a microscope and focused onto the sample, typically through a 50X objective. The reflected beam travels back along the same optical path and is rotated again by the Faraday rotator an additional 45 degrees such that at the polarizing beam splitter cube it is rotated 90 degrees relative to the same beam before its first pass through the cube. In this way the incident beam is separated from the reflected beam. This reflected beam is then directed to an optical power meter. The change in reflectance $\Delta R/R$ was determined by measuring the reflectance before (R_{before}) and after (R_{after}) the heating pulse and normalizing the difference to R_{before} so that $\Delta R/R = (R_{after} - R_{before}) / R_{before}$. The data retention was measured on as-deposited amorphous films by measuring the sample reflectance in 25 locations (5 by 5 matrix with 3 μm spacing). The sample was then heated in a furnace for a given time and at a given temperature, removed from the furnace, and reflectance was measured again in the same 25 spots. The normalized change in reflectance was assumed to be a measure of crystallization. Sample reflectance increased at certain annealing temperatures and times indicating onset of crystallization. When the reflectance did not increase any further at high temperatures and for long times the sample was assumed to be fully crystallized. The maximum observed $\Delta R/R$ for our as-deposited films was 30.7 %. This is comparable to the change in reflectance we measured when we exposed the films to heating laser pulses that led to crystallization (30.0 %). The laser tester experiments on as-deposited amorphous films were complimented by resistivity vs. time measurements at constant, elevated temperature. These isothermal measurements were performed on a custom-made four point probe set-up in nitrogen atmosphere. In this case the films were deposited on 500 nm SiO_2 on Si substrates, the $Ge_2Sb_2Te_5$ film thickness was 50 nm as well.

The data retention results obtained on as-deposited amorphous films were compared to measurements of data retention of melt-quenched amorphous material. In this case the high power laser was rastered over the sample in such a way that the overlapping heating pulses produced overlapping crystalline spots on the sample creating a square fully crystalline area. A matrix of 5 by 5 laser spots with 3 μm spacing was then written inside the crystalline area. The laser pulse was selected such that it produced a well-defined melt-quenched spot without ablation. Reflectance was measured in all spots after the melt-quenching pulse. The sample was then annealed in a furnace, removed from the furnace, and the reflectance was measured again in the originally melt-quenched spots. Alignment marks on the sample were used to relocate the sample in the original position. Measuring the reflectivity of melt-quenched spots, removing the sample from the stage and immediately relocating and aligning it on the stage again allowed for a reproducibility of the data within 5%.

Data retention was also measured using mushroom-type PCRAM cells with Ge-Sb-Te phase change material and TiN top and bottom electrodes. The bottom electrodes were fabricated using the key-hole process [10]. Each memory cell of the array is addressed by a MOSFET and the resistance is measured by the on-chip circuitry. Data retention in PCRAM cells was measured by performing a RESET operation (switching the cell in the high resistance, amorphous state) using an optimized RESET current and measuring the resistance of each cell. The chips were then annealed in a furnace for a given time and resistance of the cells was measured again after annealing. A RESET pulse width of 100ns was used for RESET operation.

3. RESULTS & DISCUSSION

As-deposited, amorphous films

As a benchmark we measured the crystallization behavior of as-deposited films using laser testing and resistivity vs. time measurements at elevated temperature. Figure 1 shows the normalized change in reflectance as a function of annealing time at a temperature of 132 ºC. In comparison Figure 2 shows the normalized resistivity as a function of temperature, both are normalized to the maximum change in reflectance/resistivity, respectively. The data points are fitted to a function of the form $1 - \exp-(t/\tau)^a$. This function has been employed to investigate crystallization using the Johnson-Mehl-Avrami-Kolmogorov analysis [11], but is has been pointed out before that in particular for laser testing this analysis has limited validity because the processes are far from thermal equilibrium [12].

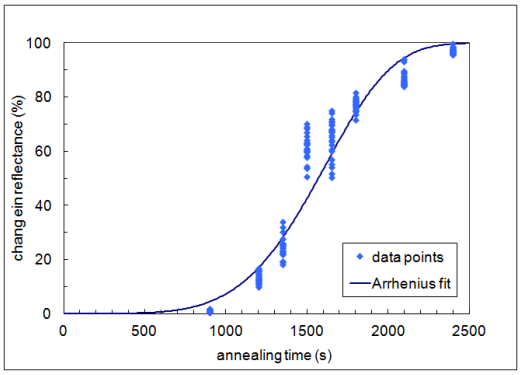

Figure 1: Normalized change in reflectivity as a function of annealing time for 132 ºC.

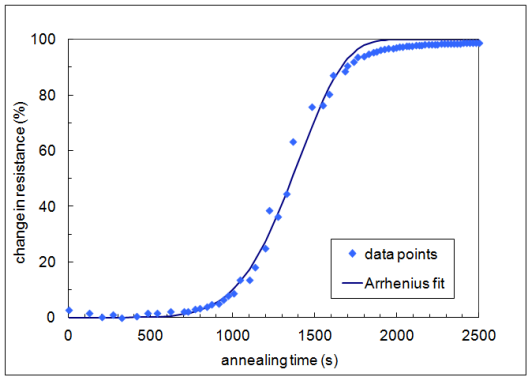

Figure 2: Normalized change in resistivity as a function of annealing time for 132 ºC.

It is probably a fair assumption that reflectance in our experiments scales linearly with the amount of the crystal fraction. For resistivity measurements this is not so obvious since a small percolating path between the contacts can lead to a large drop in resistance while the majority of the film is still amorphous. In any case, we find relatively good agreement between the reflectance and the resistivity measurements taking into account that the heating temperature profiles were not fully identical because the laser samples were annealed in a different furnace than the resistivity tester. The various data points at each temperature in Fig. 1 correspond to the 25 points measured. We can see that the distribution is pretty narrow for as-deposited amorphous material at short times, and fully crystallized material, at long

times. For intermediate times we observe a much wider distribution due to the fact that the laser pulse sometimes hits still amorphous material and sometimes already crystallized material. This is illustrated in the next Figures. Figure 3 shows the alignment marks on as-deposited amorphous films. The box was created by scanning the pulsed laser beam with high repetition rate on the sample, forming crystallized bright lines. The size of the box is 23x23μm. The image is contrast enhanced for better visibility, the actual contrast is about 30% as mentioned before. Figure 4 shows the same sample after annealing at 132 ºC for 25 min, again contrast enhanced for better visibility. The partial crystallization is obviously visible and can explain the spread in the data in Fig. 1 for times when the sample has become partially crystalline. The probe laser spot is approximately the diameter of the crystalline lines since probe and pump laser are directed to the sample through the same fiber and optics. For fully crystallized samples the box disappeared. Only the ablated spots at the corners of the box where the pump laser remained for longer times were still visible and served for sample aligning. One of these spots is indicated by an arrow in Fig. 4.

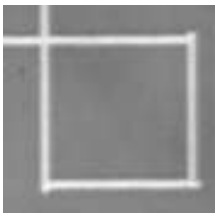

Figure 3: Crystalline box drawn on the amorphous, as-deposited sample by rastering the pump laser over the sample.

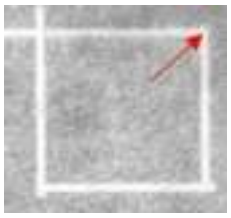

Figure 4: The same sample after annealing for 25 min at 132 ºC. The partial crystallization is well visible.

Melt-quenched, amorphous dots

Figure 5 (a) shows the crystalline square area written into the as-deposited, amorphous film. The reflectance of the laser-produced crystalline material was very comparable to crystalline material after furnace annealing. Similarly, re-crystallization times of melt-quenched dots written in laser-crystallized and furnace-crystallized material were very similar, so that we can assume that the laser- and furnace-crystallized materials are very similar.

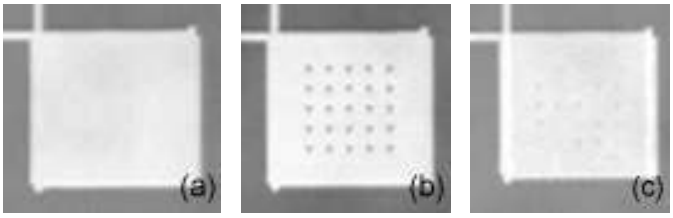

Figure 5: (a) Crystalline square are in as as-deposited, amorphous film. (b) Melt-quenched dots written by a 70 ns pump pulse. (c) Melt-quenched dots partially disappear after heating to 100 ºC for 25 min.

Figure 5 (b) shows the melt-quenched dots in the crystalline box. In this case the contrast is not as strong as the full contrast between amorphous and crystalline material because the melt-quenched dots are smaller than the probe laser spot diameter so that it measures the melt-quenched dots plus a fraction of the surrounding crystalline material. The resulting maximum contrast is about 14 %. After annealing for 25 min at 100 ºC the dots have become brighter because of partial crystallization, and some of them have disappeared completely, see Fig. 5 (c). For longer annealing or higher temperatures all dots disappeared completely.

Figures 6 compares the change in reflectance for as-deposited, amorphous and melt-quenched, amorphous Ge-Sb-Te. It is clear that that the reflectance of the melt-quenched Ge-Sb-Te increases at much lower temperature than as-deposited Ge-Sb-Te. From results on as-deposited Ge-Sb-Te one would predict very good data retention at 90 and 100ºC while from the data on the melt-quenched spots one would predict failure times in the range of minutes.

PCRAM devices

PCRAM devices were programmed in the RESET state and resistance was measured after baking at 90 ºC and 100 ºC for various times. Figures 7 and 8 show the SET and RESET resistance distributions before annealing (ini) and the resistance distributions after the annealing cycles for different durations. It is evident that heating at these temperatures has a large effect on the RESET resistance distributions. At 90 ºC many initially RESET bits have resistances below 10^2 kOhm so there is already an overlap of the SET and RESET/annealed resistance distributions.

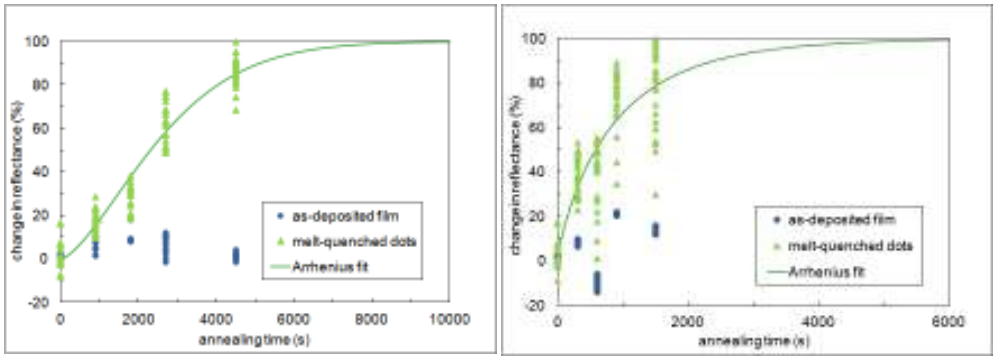

Figure 6: Change in reflectance of as-deposited, amorphous and melt-quenched, amorphous Ge-Sb-Te as a function of annealing time at 90 (left) and 100 ºC (right).

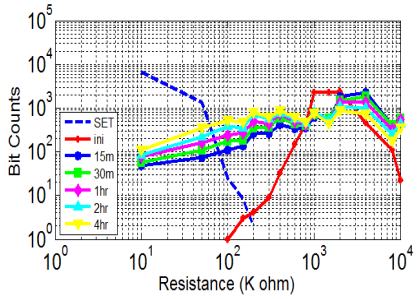

Figure 7: Change in resistance distribution of originally RESET PCRAM cells after baking at 90 ºC for Sb-rich Ge-Sb-Te material.

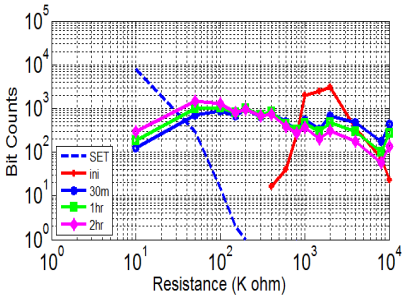

Figure 8: Change in resistance distribution of originally RESET PCRAM cells after baking at 100 ºC for Sb-rich Ge-Sb-Te material..

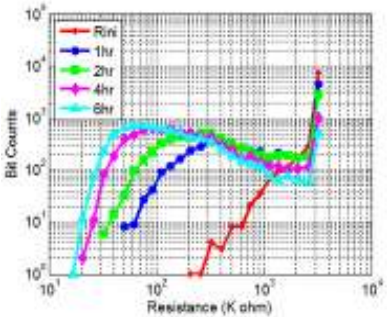

Figure 9: RESET resistance distribution after heating at 190 ºC for up to 6h for Ge-rich Ge-Sb-Te material.

For the 100 ºC annealing the resistance distribution has become very wide and the center of the RESET/annealed distribution is now even closer to the SET distribution. The data loss is severe. These results are in good agreement with the measurements of the reflectance of melt-quenched, amorphous laser spots. They show a large widening of the distributions and a shift to lower resistance and higher reflectance, respectively, for annealing temperatures as low as 90 ºC, while 90 ºC annealing of as-deposited, amorphous films leads to no measurable change in reflectance.

We used this new methodology to measure data retention in blanket films as a prediction for data retention in PCRAM devices to improve the properties of the phase change material in this aspect. Figure 9 shows the data retention of PCRAM devices using an improved Ge-rich GeSbTe212 material [13]. This material has a crystallization temperature of about 250 ºC and has much improved data retention behavior. Even though the PCRAM cells were heated to a very high temperature of 190 ºC the majority of the cells remain in the high resistance RESET state, just a small fraction of tailbits have drifted to lower resistance.

4. CONCLUSIONS

Combined static laser tester, resistivity measurements on blanket films and on PCRAM devices have shown that measurements on as-deposited films greatly overestimate predictions for data retention in PCRAM devices. Estimates of data retention obtained from melt-quenched, amorphous Ge-Sb-Te material are a much more accurate way to predict data retention in devices. Even though it is difficult to compare experimental conditions exactly, due to the different nature of the amorphization conditions in laser testing and devices, the temperature range for device failure is much closer to the temperature range for data loss for melt-quenched, amorphous Ge-Sb-Te compared to as-deposited, amorphous Ge-Sb-Te. This new testing methodology enables us to optimize phase change materials on blanket films for better data retention in PCRAM devices.

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