Experimental report

31/03/2020

Proposal: **6-05-990** **Council:** 4/2017

Title: Study of the phase separation in GexTe100-x amorphous films

Research area: Materials

This proposal is a resubmission of 6-05-984

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Samples: GexTe100-x with x=12, 20, 27, 30, 37, 42, 48

Instrument	Requested days	Allocated days	From	To
D16	5	5	25/05/2018 13/06/2018	28/05/2018 18/06/2018

Abstract:

Storage density is a key-issue in the field of information storage. Storage densities in PC-RAM memories could be drastically increased thanks to phase-change materials that could offer the possibility of making multi-level cells. Changing its amorphized volume could systematically alter the cell resistance. This process requires, however, a stable amorphous state, i.e., a material with a time-independent resistance. This effect, commonly denoted as resistance drift, may cause severe data corruption over time and thus hampers the realization of multi-level phase change memories.
We recently combined the amorphous state resistivity measurements to structural and thermal analyses in amorphous GexTe100-x films. Our results allow us to identify two singularities, which could be linked to a phase separation in films with x > 25 or x > 35 at.% Ge. In this context, we propose to extend the structural investigations of the Ge-Te system by exploring possible structural rearrangement using small angle neutron scattering (SANS). These measurements will help to understand the ageing of the Ge-Te films, which could be interesting in the operation mode of electrical memories.

Study of the phase separation in Ge_xTe_{100-x} amorphous films

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Abstract

Storage density is a key-issue in the field of information storage. Storage densities in PC-RAM memories could be drastically increased thanks to phase-change materials that could offer the possibility of making multi-level cells. Changing its amorphized volume could systematically alter the cell resistance. This process requires, however, a stable amorphous state, i.e., a material with a time-independent resistance. This effect, commonly denoted as resistance drift, may cause severe data corruption over time and thus hampers the realization of multi-level phase change memories.

We recently combined resistivity measurements and structural and thermal analyses in amorphous Ge_xTe_{100-x} films. Our results allowed to identify two singularities, which could be linked to a phase separation in films with x > 35 at.% Ge.

In this context, we proposed to extend the structural investigations of the Ge-Te system by exploring possible structural rearrangement using small angle neutron scattering (SANS). These measurements aimed at helping to understand the ageing of the Ge-Te films, which could be interesting in the operation mode of electrical memories. This experiment was a continuation of the experiment carried out on D11 instrument in February 2017 (proposal 6-05-984).

Experimental Details

Five glasses of nominal compositions $Ge_{15}Te_{85}$, $Ge_{20}Te_{80}$, $Ge_{27}Te_{73}$, $Ge_{30}Te_{70}$ and $Ge_{48}Te_{52}$ were prepared by thermal co-evaporation of 5N (99.999% purity and metallic impurities <200 ppm) germanium chips (Aldrich) and 4N5 (99.995% purity) tellurium powders (5NPlus) (for more details on sample preparation refer to Refs. [1]). The powders used for SANS measurements were obtained by scraping the previously deposited films.

Small Angle Neutron Scattering (SANS) was carried out at D11 instrument at the Institute Laue-Langevin in Grenoble (France). The wavelength was set to 4.5 Å and two different instrument configurations (WANS and SANS) were used to cover a Q range from 2.10^{-2} to 2.3 Å^{-1}. Ge_xTe_{100-x} samples were placed in non-sealed cylindrical vanadium containers with an inner diameter of 4 mm (Figure 1).

The required ancillary measurements, *i.e.* vanadium rod (5 mm in diameter), empty cell and cadmium with dimensions as close as possible to that of the sample, were also carried out. Measurements were carried out at room temperature.

The raw scattering data were corrected for the electronic background and empty cell and were normalized on the absolute scale in cm^{-1} using the attenuated direct beam to calculate the incident flux and using the ILL Lamp software for data reduction.

Figure 1: *Ge_xTe_{100-x} samples placed in non-sealed cylindrical vanadium containers.*

Results

Figure 2 shows the normalized SANS scattering intensities I(Q) for all Ge_xTe_{100-x} samples measured at room temperature. All curves exhibit a similar behavior constituted of two peaks at high-Q values and a regime with a linear increase (in log-log) at low-Q values. However, some differences can be observed when the germanium content is increasing in the glass.

In the low-Q range [2.10^{-32}? Å^{-1}, 2.10^{-1} Å^{-1}], it is interesting to note that the samples can be divided into three different groups. A first group composed of $Ge_{15}Te_{85}$ and $Ge_{20}Te_{80}$ glasses (Ge-low region), a second group composed of $Ge_{27}Te_{73}$ and $Ge_{30}Te_{70}$ glasses (Ge-intermediate region), and a third group with the $Ge_{48}Te_{52}$ sample alone (Ge-rich region).

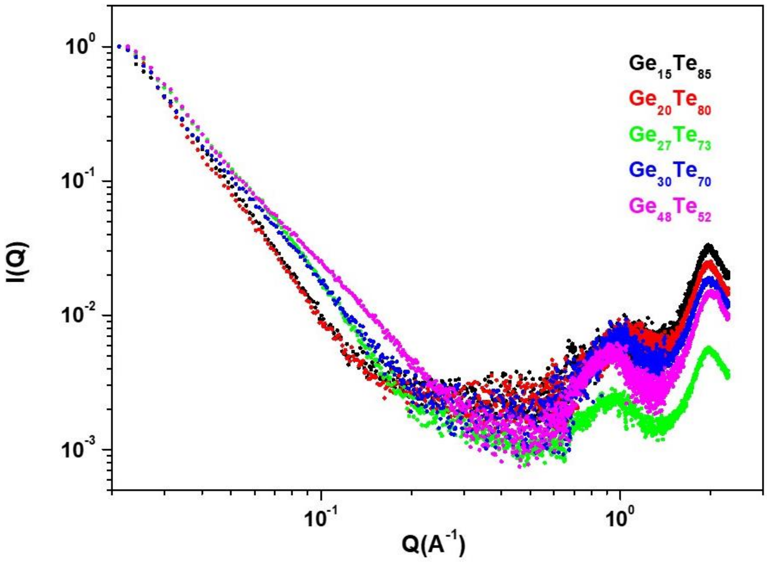

Figure 2*: Normalised SANS scattering intensity I(Q) for Ge_xTe_{100-x} glasses elaborated by co-thermal evaporation technique.*

The enlarged Porod's law, $I(Q) \approx B\boldsymbol{Q}^{-m}$, could help in gaining information on the interface between the two media (see Figure 2). Thus, the slope dI(Q)/dQ (Porod exponent) was extracted from all curves. We observe a decrease in the slope with the increase in the germanium content. The Porod exponent m varies from 3 for the Ge-low region, ~ 2.7 for the Ge-intermediate region to ~ 2.4 for the Ge-rich region. According to Porod's law, the case with m between 3 and 4 characterizes rough interfaces whereas that with m values varying between 1 and 3 corresponds to a mass fractal/dendritic behaviour. It is important to note that an abrupt boundary exists between the glass powder and the air in our experiments. Then, it is difficult to conclude on the type of interface without a deeper study.

Nevertheless, such a deeper study sounds necessary since the three identified groups are delimited by the two singularities at x = 22-25 and x-= 33-35 at. % Ge reported in ref. [2].

In the high-Q range [0.5 $Å^{-1}$, 2.3 $Å^{-1}$], the shapes of the five curves are very similar with only some changes in the intensity and positions of the main features (Figure 3). One can note a first sharp diffraction peak (FSDP) at about 1 $Å^{-1}$ with a slight decrease in Q_{FSDP} position with the Ge content. Also, we observe a first principal peak at about 2 $Å^{-1}$, which does not show significant changes with the composition of the glass.

These results are in agreement with neutron diffraction experiments performed at the 7C2 liquid and amorphous diffractometer of LLB (Saclay, France) on the Ge_xTe_{100-x} system [3].

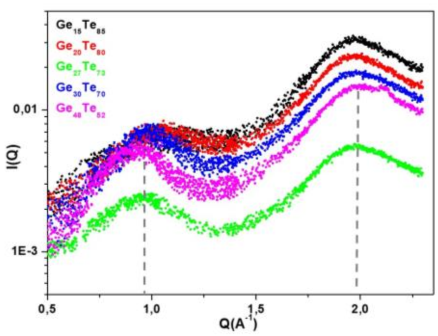

Figure 3*: Normalised SANS scattering intensity I(Q) for Ge_xTe_{100-x} glasses in the high-Q range.*

References

[1] P. Jóvári, A.A. Piarristeguy, R. Escalier, I. Kaban, J. Bednarcik, A. Pradel; « *Short range order and stability of amorphous Ge_xTe_{100-x} alloys ($12 \leq x \leq 44$)* », Journal of Physics: Condensed Matter 25 (2013) 195401.
[2] A.A. Piarristeguy, M. Micoulaut, R. Escalier, P. Jóvári, I. Kaban, J. van Eijk, J. Luckas, S. Ravindren, P. Boolchand, A. Pradel; « *Structural singularities in Ge_xTe_{100-x} films* », Journal of Chemical Physics 143 (2015) 074502.
[3] P. Jóvári, A.A. Piarristeguy, A. Pradel, I. Pethes, I. Kaban, S. Michalik, J. Darpentigny, R. Chernyshov; « *Local order in binary Ge-Te glasses – an experimental study* », Journal of Alloys and Compounds 771 (2019) 268-273.