Study of $Ge_2Sb_2Te_5$, GeTe and N-doped GeTe for application in the Phase-Change Random Access Memories (PCRAM)

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ABSTRACT

The characteristics of $Ge_2Sb_2Te_5$ (GST), GeTe and nitrogen-doped GeTe thin films deposited on W/SiO2 substrates were investigated by reflectometer, static tester and atomic force microscopy (AFM). Differential Scanning Calorimetry measurements and Differential Thermal analyses were carried out on these materials to determine their crystallization and melting temperatures. It was found that the amorphization and crystallization behaviors of these materials were different, especially that the nitrogen-doped GeTe materials show a growth-dominated crystallization behavior although GST and GeTe shows a nucleation-dominated crystallization behavior. Characteristic temperatures of these materials were determinate to estimate amorphous phase stability and reset power required to melt-quenched the materials.

Keywords: Phase-Change material, nitrogen doping, crystallization behavior, characteristic temperatures.

1. INTRODUCTION

Phase-Change Random Access Memory (PCRAM) technology, using the fast and reversible phase transition between a high-resistive amorphous phase and a low-resistive crystalline phase to store the data, is one of the most promising candidates for the next generation of non-volatile electrical memories since it offers better endurance, programming speed and scalability compared to standard Flash memories [1]. Nevertheless, PCRAM still requires high current for the transition from crystalline to amorphous phase. Electrothermal confinement of the phase-change material must be improved. Amorphous phase stability is another essential requirement since it determines the data retention of the memory. In this framework, we have investigated the characteristics temperatures of different phase-change materials and studied their crystallization behavior since it determines their crystallization ability.

2. EXPERIMENTS

100 nm-thick GST, GeTe and nitrogen-doped GeTe full-sheet depositions were fabricated by Physical Vapor Deposition (PVD) from a monotarget and nitrogen flux for nitrogen-doped GeTe at room temperature. Materials are obtained in the amorphous phase. In order to screen the effect of nitrogen addition, several compositions were deposited. Their percentages are revealed by Rutherford Back-scattering (RBS) measurements. Materials are amorphous after the deposition. Crystallization temperatures were determined with a reflectometer which allows following the reflectivity evolution of the sample during thermal annealing under Argon atmosphere. Reflectivities are plot versus temperature and the increase of the curve is directly related to the phase change, i.e. amorphous to crystalline transition.

Laser-induced amorphization and crystallization were conducting using a 405 nm pulsed-heating laser. The laser is focuses on the sample and reflected light is directed to a photodiode detector. Reflectivities measured before and after the laser pulse are collected by the computer. Optical contrasts are plotted versus power and duration of the laser pulse. Amorphization and crystallization cartographies are so obtained for each material. Differential scanning calorimetry measurements were done under nitrogen flux with a 2920MDSC V2.6A TA Instruments and differential thermal analyses with DSC 404 NETZSCH.

3. RESULTS AND DISCUSSION

GST, GeTe and nitrogen-doped GeTe reflectivities measurements were performed with the reflectometer. Each curve was obtained during heating from ambient temperature to 400°C at a fixed rate of 10°C.min^{-1}.

It is observed that the crystallization temperature of GeTe is higher than that of the material GST. An increase of the crystallization temperature as a function of nitrogen doping is also, clearly, observed. It can therefore be said that nitrogen stabilizes the amorphous phase and delays the crystallization process. However, this phenomenon is not completely understood. Nitrogen-doping of GeTe crystalline powder and other XRD experiments at the European Synchrotron Radiation Facility (ESRF) are still in progress to enlighten us on the involved phenomena.

GST, GeTe and nitrogen-doped GeTe amorphization cartographies were performed with the pulsed-heating laser. It can be observed that amorphization of GST compound requires nearly the same energy than GeTe. Contrariwise, the higher the nitrogen content, the higher is the required amorphization energy. *Figure 1* shows the thermal analyses of the different materials. Crystallization temperatures are obtained for each material and are similar to those obtained with the reflectometer. It is clearly observed that the melting temperature of GST is smaller than the melting temperature of GeTe. This is in accordance with the fact that melt-quenching amorphization of GST requires less energy that GeTe. However, it can also be observed that melting temperatures of doped-GeTe are almost the same as GeTe and independent of nitrogen-doping. Moreover, thermal absorption coefficients are also quite the same for GeTe and doped-GeTe. So it appears that nitrogen-doping of GeTe leads to a harder amorphization of the materials. Crystallization cartographies of the different materials were also performed with the pulsed-heating laser. It can be observed that crystallization of GST and GeTe is difficult. The reflectivity contrast remains between 0,3 and 0,5 (note that a complete crystallization is achieved for an optical contrast equal to 1). Nitrogen-doping leads to better crystallization with values higher than 0,7. It can be noted that materials with low nitrogen content crystallize better but slower than with higher nitrogen content. However, comparisons between the different materials are done for equivalent optical contrast. To better compare them, atomic force microscopy measurements were done to determinate the size of the amorphous marks obtained after a known laser pulse (power and duration). Experiments are still in progress and will-allow us to conclude on the impact of nitrogen-doping on the crystallization speed.

Focus on the crystallization mechanism of the different material was also done, based on a previous study [2]. We have tried to determinate if the recrystallization process is growth-dominated or nucleation-dominated. When crystallization is nucleation-dominated, it is known that, regardless the amorphization power applied and consequently the amorphous marks size, crystallization starts for the same crystallization power. In opposite, when the crystallization mechanism is growth-dominated, higher power is required to crystallize wider amorphous areas. *Figure 2* shows different graph presenting crystalline fraction plot versus crystallization pulse power. Each curve represents one amorphization condition (i.e. laser pulse power and duration). It can be observed that GST and GeTe present the same behavior: regardless the amorphization power, crystallization appears for the same crystallization power. In contrary, nitrogen-doped GeTe presents a growth-dominated crystallization mechanism since the crystallization powers required to crystallize the material vary as a function of marks sizes (namely the amorphization power). Few are known about the incorporation of nitrogen in GeTe and how this incorporation affects the crystallization mechanism. Therefore, XRD in-situ measurements are still in progress to try to understand this phenomenon.

4. CONCLUSION

To conclude, we have studied different phase-change materials, namely GST, GeTe and nitrogen-doped GeTe. These materials present very different crystallization temperature but very close melting temperatures, excepted for GST. Amorphization cartographies show that nitrogen-doping increase the energy required to melt-quenched the material. According to our preliminary experiments, mechanism of crystallization seems to be nucleation-dominated for GST and GeTe and growth-dominated for nitrogen-doped GeTe. Some experiments are still in progress to shed light on this phenomenon.

REFERENCES

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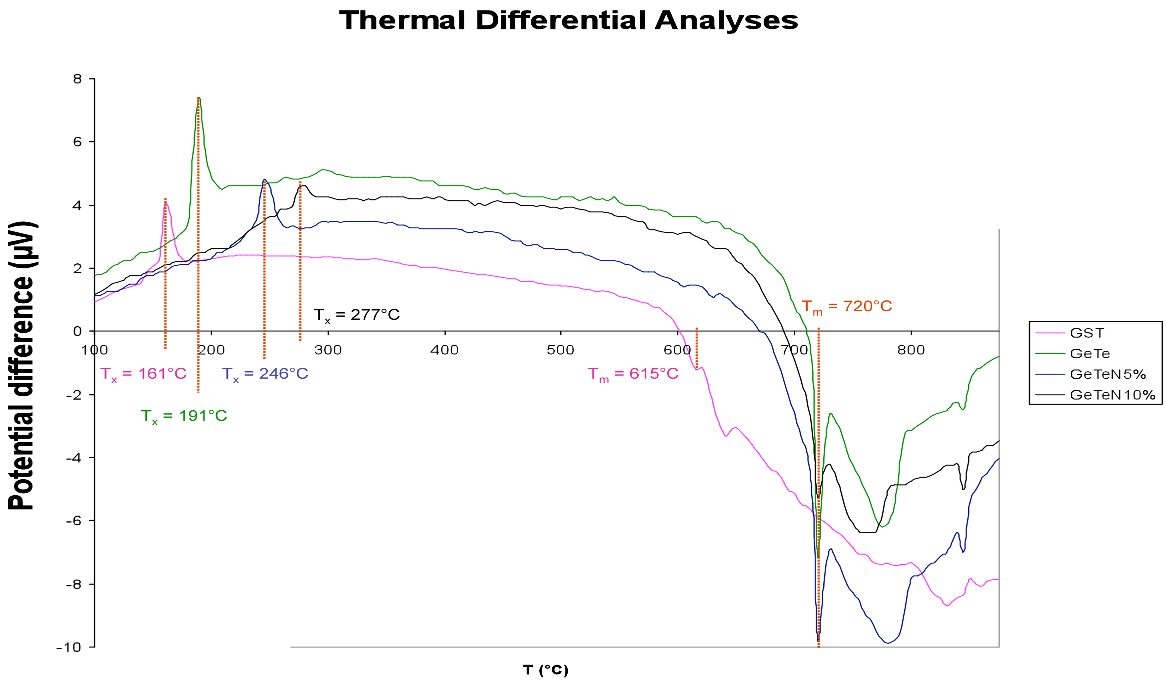

Figure1: Differential Thermal Analyses of GST, GeTe and two nitrogen-doped GeTe. The crystallization temperatures and melting temperatures are reported on the graph.

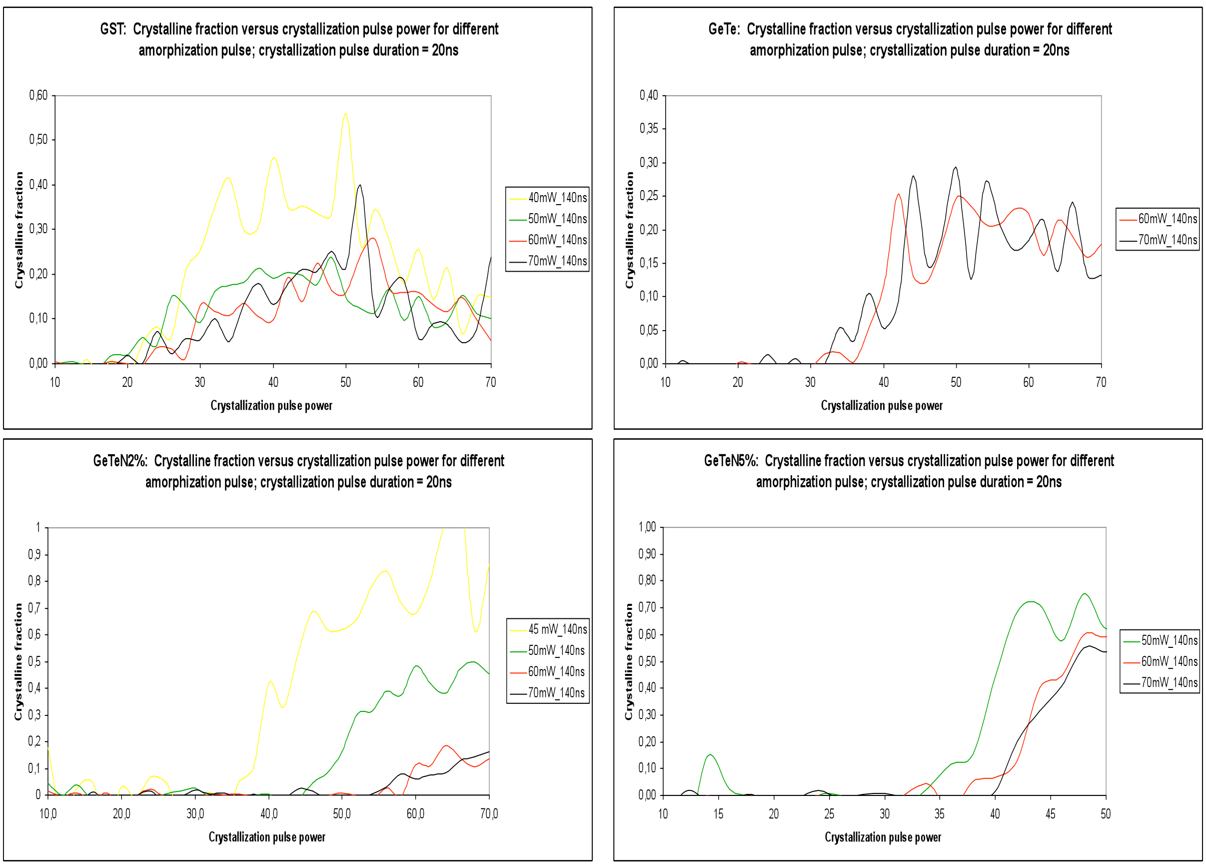

Figure 2: Crystalline fraction versus crystallization pulse power for different amorphization pulse for GST, GeTe and two nitrogen-doped GeTe.

Biographies

“Jean-Claude BASTIEN” is a student doctor of the « Commissariat à l’énergie atomique et aux énergies alternatives » (CEA[2]), France and the « Laboratoire Verres et Céramiques » of the « Université de Rennes1 », France. His PhD thesis is in the field of the PCRAM, especially on the crystallization process of the phase-change materials. He received a Bachelor’s degree and a Master Degree in chemistry and solid state chemistry respectively at the “Université de Rennes1”, France. He prepares its graduates to obtain the doctoral degree in chemistry.