

GeTe-based Phase Change Memories: Effect of stoichiometric variations and N or C addition

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ABSTRACT

In this paper, we report on the properties of GeTe-based phase change materials. Stoichiometric variations ranging from 30 to 70 at% Ge show that the best programming characteristics in terms of set speed and set/reset states stability are obtained close to the 50/50 composition. Meanwhile, reset current reduction and improved retention properties are obtained in the Te-rich domain. Our study further shows that additions in the extent of a few percents of N or C in the stoichiometric compound $\text{Ge}_{50}\text{Te}_{50}$ allow improving the amorphous phase stability. While the programming characteristics of the devices are unchanged when adding N, addition of C leads to a lower reset current but also a decreased set speed.

Key words: Phase Change Memories (PCM), GeTe, GeTeN, GeTeC.

1. INTRODUCTION

Phase Change Memory (PCM) is one of the most promising concepts for the future generations of Non Volatile Memories. Several decades focused on technological developments have led to the set-up of highly competitive PCM demonstrators [1, 2]. Extensive work is nowadays performed on the Phase Change Materials to optimize the cell properties for specific applications. In particular, for the embedded memory market, it is desirable to reduce the writing current while automotive applications require enhancing the high temperature data retention. In this paper, we propose an extensive study of GeTe-based phase change materials and memory cells, based on results previously reported [3-12]. The effects of stoichiometric variations $\text{Ge}_x\text{Te}_{1-x}$ and N or C addition have been considered. The crystallization temperature and activation energy for crystallization of the materials have been evaluated from optical reflectivity or electrical resistivity measurements on thin films deposited by RF sputtering. The structure of the materials has been identified with XRD and Raman characterization. As for the memory cell characterization, the reset current, set speed, and data retention properties have been evaluated on simple pillar type-resistor.

2. Effect of stoichiometric variations Ge_xTe_y

The first part of our study is devoted to the characterization of Ge_xTe_y materials and memory cells, ranging from 30 to 70 at% Ge. The optical reflectivity and electrical resistivity measurement versus temperature show that the crystallisation temperature and activation energy for crystallisation reaches a minimum around the $\text{Ge}_{50}\text{Te}_{50}$ stoichiometric composition. XRD characterisations reveal that the $\text{Ge}_{50}\text{Te}_{50}$ compound crystallises in the rhombohedral phase, this phase appearing together with respectively cubic Ge and hexagonal Te when departing from the stoichiometric composition toward the Ge-rich or Te-rich domain. We show that this phase separation is accompanied by an instability of the set/reset states for the Ge-rich compositions, which are hereafter not suitable for PCM applications. In the Te-rich domain and in agreement with the resistivity measurement, the programming curves measured on basic memory cell show that $\text{Ge}_{30}\text{Te}_{70}$ composition exhibits the highest resistance window, together with a decrease in reset current of about 25%. However, the set-reset programming curve also shows that this composition corresponds to the lowest Set speed. Retention measurements confirm that the $\text{Ge}_{50}\text{Te}_{50}$ composition has the lowest thermal stability while $\text{Ge}_{30}\text{Te}_{70}$ can achieve a fail temperature after 10years of 127°C. Endurance up to 10^7 has been

demonstrated for all Te-rich composition, morphological analysis showing voids and W plug surface roughness appearing after failure for the $\text{Ge}_{50}\text{Te}_{50}$ composition. Finally, we show that the drift is not impacted by the stoichiometry change, while both the threshold and holding voltage increase with increasing Te content.

3. Effect of N or C addition in $\text{Ge}_{50}\text{Te}_{50}$

After showing that $\text{Ge}_{50}\text{Te}_{50}$ exhibits the best programming characteristics but a retention still not coping with targeted specifications for automotive applications, we present the effect of N and C addition in this compound.

With the addition of N in $\text{Ge}_{50}\text{Te}_{50}$, optical reflectivity and electrical resistivity measurements show an increase of both the crystallization temperature and activation energy with N content. XRD and Raman spectra reveal that the crystallized phase turns to be cubic for N content above ~4%, while the grain size is reduced and the Ge segregation is suppressed. Meanwhile, XPS results show evidence for Ge-N bonding, leading us to the conclusion that amorphous GeN domains subsist after the crystallization of GeTe. As for the programming characteristics, the reset current and the set speed remain unchanged, while the retention properties are largely improved, with a fail temperature after 10years of 154°C for 2% of N. Drift is unchanged, while holding voltage is increased.

The addition of C in $\text{Ge}_{50}\text{Te}_{50}$ also leads to an increase in crystallization temperature and activation energy for crystallization. Again, the C content above ~4% leads to the crystallization of a cubic phase, with an increased disorder and a grain size reduction following the addition of C. Unlike the addition of N, the addition of C impacts the programming characteristics, decreasing the reset current by about 30% but also slowing down the set speed. As expected from materials characterizations, the retention is improved resulting in a fail temperature after 10years of 127°C for 10% of C.

4. CONCLUSION

In this paper, we have shown how the GeTe-based PCM device performances can be tuned thanks to materials engineering. GeTe host material features Reset current reduction either in the Te-rich domain or with addition of C within $\text{Ge}_{50}\text{Te}_{50}$, which is however accompanied by a set programming time increase. These material modifications, in a similar way like N addition, also feature improved data retention.

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Biography

Véronique Sousa graduated in 1994 from the Institut National Polytechnique de Grenoble (INPG) in the field of Materials Science and Engineering. During her PhD, which she received in 1997 from the INPG, she worked on the experimental and fundamental aspects of magnetic thin films with perpendicular anisotropy and spent a 3 months stay at the Electrotechnical Laboratory, in the group of Prof. Katayama, to work on magneto-optics. Afterwards, she took a one-year post-doctoral position at INESC in the group of Prof. P. Freitas, and worked on various thin film materials used for magnetic data storage devices such as permanent magnets, spin valves or tunneling junctions. Since October 1998, she is working at CEA-Leti-MINATEC-Campus where she first focused on the development of advanced magneto-optical and phase change materials for optical data storage. Hereafter, she managed several projects aiming at the optimization of chalcogenide materials for various solid state memory technologies, including Current Bridging RAM and Phase Change Memories.