Temperature driven structural evolution of Ge-rich GeSbTe alloys and role of N-doping

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ABSTRACT

We present the investigation of the structure of undoped and N-doped Ge-rich GeSbTe alloys as a function of the annealing temperature. We highlight the stability of $SbTe_3$ features of GeSbTe phase and the progressive rearrangement of Ge-Te units around these stable units. Moreover, we investigate the role of N-doping and the impact of formed Ge-N bonds on the overall crystallization mechanism in these Ge-rich GeSbTe alloys.

Key words: Phase-change material, Ge-rich GeSbTe alloys, N-doping, structure, crystallization

1. INTRODUCTION

Phase-change memory (PCM) technology is shown to be the most mature candidate among Non-Volatile Memory technologies. The maturity of PCM has been demonstrated by its recent commercialization in Storage Class Memory Applications [1]. Moreover, thanks to the material engineering of GeSbTe alloys, in particular by Ge enrichment and N-doping, PCM demonstrated an improved reliability at high temperature fulfilling the strict requirements of Automotive Applications [2][3]. We report on the structure of as-deposited and annealed Ge-rich GeSbTe alloys in order to contribute to better understanding of the structural mechanisms during the crystallization of these alloys and the effect of N-doping.

2. EXPERIMENTAL

Amorphous Ge-rich GeSbTe (GGST) layers were prepared by magnetron sputtering from Ge and $Ge_2Sb_2Te_5$ (GST225) target. The N-doped layers with two different N contents (GGSTN, GGSTN$^+$) were prepared by the same method in Ar/N_2 gas mixture in deposition chamber. An ultrathin capping layer was deposited on the layers surface to avoid the oxidation effect. The ex-situ annealing in the temperature range from 200 °C to 450 °C was performed in N_2 inert atmosphere. The structure of as-deposited and annealed samples was investigated by Raman and FTIR spectroscopy and X-ray diffraction (XRD).

3. RESULTS & DISCUSSION

Raman spectra of as-deposited and annealed GGST layer are shown in **Fig. 1**. The spectra can be divided into 2 parts: vibrational modes of GeSbTe phase at 100-190 cm^{-1} and vibrational modes of Ge (amorphous a-Ge and crystalline c-Ge) at 190-300 cm^{-1} [4]. Raman spectra reveal the stability of $SbTe_3$ modes of GeSbTe phase up to high temperatures. Low wavenumber region, assigned to GeTe modes in various configurations ($GeTe_{4-n}Ge_n$, where n = 1, 2), shows a significant evolution as the temperature increases (**Fig. 2**). The first decrease is assigned to the primary reorganization GeTe bonds, related to slight expulsion of excess Ge from the GeTe units. Further, GeTe modes intensity increases up to 350 °C, forming the stable GST225-fcc phase. Simultaneously, the a-Ge modes progressively evolve towards the c-Ge modes starting from 335 °C. The appearance of GST225-fcc phase and c-Ge phase at 350 °C was confirmed by XRD. Investigation of the N-doped GGST layers showed the same structural evolution; however, the changes are shifted to higher temperatures. N-doping in GGST leads to the formation of Ge-N bonds in the structure (confirmed by FTIR spectroscopy). Formation of the Ge-N bonds delays the reorganization of GeTe bonds (**Fig. 2**). As a result, all the consequent processes in the layers, i.e. GST225-fcc phase crystallization, Ge segregation and Ge phase crystallization are also shifted to higher temperatures. The order of

the steps during the structural evolution of GGST and the delay caused by N-doping are summarized in **Fig. 3**.

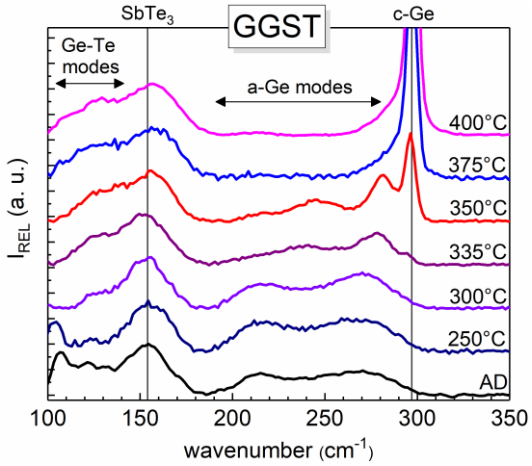

Fig. 1: Raman spectra of as-deposited (AD) and annealed layers of GGST.

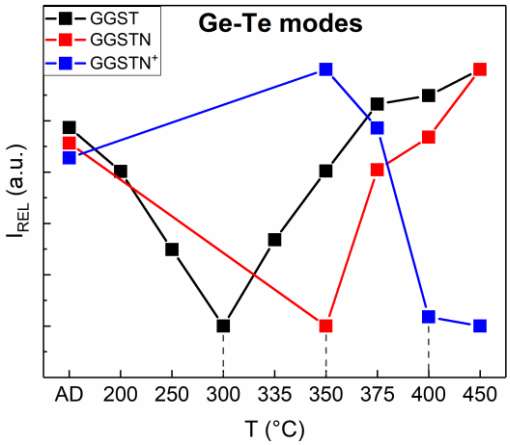

Fig. 2: Evolution of the GeTe modes intensity from Raman spectra as a function of temperature for GGST and N-doped GGST.

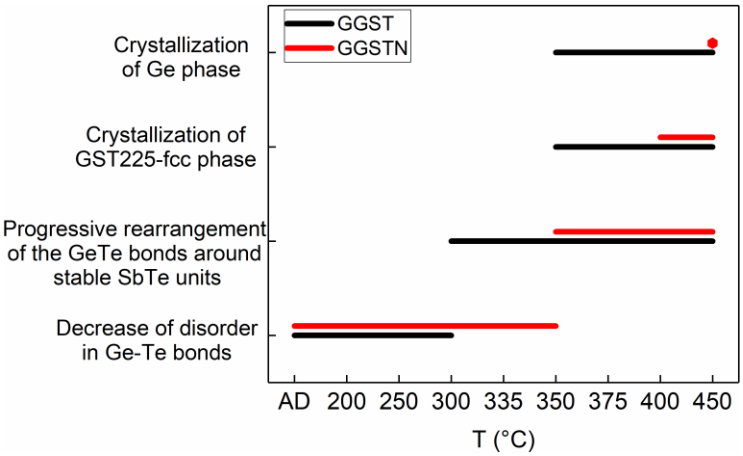

Fig. 3: Diagram summarizing the steps during the structural evolution of GGST and GGSTN.

4. CONCLUSIONS

The investigation of GGST alloys by Raman spectroscopy has revealed the stability of $SbTe_3$ units up to high temperatures. The $SbTe_3$ units thus form the main feature of GeSbTe phase. The progressive rearrangement of GeTe units around stable $SbTe_3$ is observed. The Ge in excess is progressively expulsed and the separated Ge and GST225-fcc crystalline phases are formed. N-doping of the GGST leads to the formation of Ge-N bonds, which result in delaying the GeTe bonds reorganization to higher temperatures. Therefore, all following processes of the overall crystallization mechanism, i.e. Ge expulsion, Ge and GeSbTe phase separation and the crystallization of both phases are also delayed to higher temperatures.

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