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Structural changes in doped $Ge_2Sb_2Te_5$ thin films studied by Raman spectroscopy

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Abstract

In this study, we investigated $Ge_2Sb_2Te_5$ (GST225) amorphous thin films doped with Bi, Sn and In, using Raman scattering spectroscopy, to obtain information about structural changes after doping. Such impurities as Bi and Sn were chosen due to their isomorphism with one of the main components; indium is an active dopant for phase change materials. Two main, most intensive bands appeared at 125 and 153 cm^{-1} in the spectrum of undoped amorphous GST225 thin film. Additional small bands in the range of 80 cm^{-1} and near 300 cm^{-1}, which disappeared in Raman spectra of crystalline GST225 thin films, were also observed. The obtained peak parameters were found to correlate with the dopant type and concentration. The concentration dependencies are not monotonic, and this fact indicates different incorporation mechanisms for different dopant levels.

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Keywords: Raman scattering spectroscopy; chalcogenide thin film; GST225; phase change memory; doping

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1. Introduction

Chalcogenide-based phase change memory (PCM) materials have been widely used for optical data storage [1] and now are finding application in electronic non-volatile memory (NVM) devices [2]. Among typical PCM materials, the greatest attention of researchers involves compositions that lie on the pseudobinary line $GeTe\text{-}Sb_2Te_3$ (GST), since these materials enabled phase change optical storage technology [3]. Ternary alloy $Ge_2Sb_2Te_5$ (GST225) is a stoichiometric compound which has two crystalline phases (metastable rock-salt phase and high temperature layered trigonal phase). The compound can be obtained in an amorphous phase using different deposition methods: thermal evaporation of synthesized materials in vacuum [4, 5] and rf-magnetron sputtering [6, 7]. Both methods have their advantages and disadvantages. One of the advantages of thermal evaporation is the ability to deposit thin films of different compositions promptly without advance preparation of the targets for each composition. In addition, the homogeneous Ge-Sb-Te thin films, with small area, can be easily obtained by varying the technological parameters of evaporation, e.g. the evaporator temperature, the substrate temperature, the sample mass and etc. The need to improve PCM technology requires effective methods for controlling the physical properties of the material. One of the main ways to alter characteristics is the introduction of a new component, which is accompanied by a solution of impurity in matrix. However, most of chalcogenide glassy semiconductors are insensitive to doping because of the "8-N" rule [8]. In this case, the control of the electrical and optical properties of the PCM materials transforms into a complex problem. One of the possible effective ways of solving it, is to use isomorphic elements as impurities. For GST system, bismuth and tin can be used for this purpose. Indium is also a good choice as a dopant since recently it was reported that the introduction of indium into GST225 increased optical contrast and changed the crystallization speed [9]. It was shown in [9, 10, 11] that the concentration of modified impurities was several atomic percents. Such amounts of dopants are sufficient to change the phase transformation parameters of GST225, while the phase separation of the material has not been observed. In this article, we focus on the investigation of doped amorphous GST225 thin films using Raman spectroscopy. The influence of Bi, Sn and In doping on bonding configuration is analyzed by comparison with undoped GST225 thin film.

2. Experimental procedures

The initial $Ge_2Sb_2Te_5$ alloys doped with different amounts of Bi, In and Sn (0.5, 1 and 3 wt.%) were prepared using the synthesis method described in [12]. The materials (99.99% purity) were sealed in evacuated ($5\cdot10^{-3}$ Pa) quartz ampoules, then heated step by step to 850^0C in a rocking furnace to ensure the melt was homogeneous. Thin films were prepared using thermal deposition from these doped GST225s on c-Si (100) substrates in a vacuum chamber. Residual pressure in the chamber was 10^{-4} Pa. The maximum temperature during evaporation was kept below 630^0C. The area of the thin films, not in excess of 1x1 sq. cms, had two benefits: made it possible to carry out the Raman measurements and ensured the thin films homogeneity.

The films thickness was determined from the height of step using AFM scan (NT-MDT SolverPro). The morphology of the layers was studied by SEM (Carl Zeiss NVision 40). The phase of the obtained amorphous thin films was determined by XRD (Rigaku D/MAX, Cu K_α λ=0.15481 nm). Rutherford backscattering (RBS) (E_d=1.0 and E_α=2.7 MeV at 135^0 scattering angle), X-Ray Microanalysis (CAMEBAX, the accuracy of ±2%) and XRF (X-Art M scanning spectrometer, the accuracy of ±2%) were used as analytical methods to determinate the thin film compositions and the element profiles across the thin films thickness. The measurements were carried out at different spots on the surface of the thin