

The effect of nitrogen doping on the structure of Ge₁Sb₂Te₄ film

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In order to increase the Ge₁Sb₂Te₄ sheet resistance, the nitrogen was used as a dopant. The effect of the nitrogen on the Ge₁Sb₂Te₄ structure film was studied using XRD and Raman spectroscopy methods. The nitrogen has a great effect on the resistance annealing behavior of Ge₁Sb₂Te₄ film by suppressing the phase transition from face cubic centered to the hexagonal closed packed structure. For high nitrogen percentage in the film, the transition temperatures were established by sheet resistance measurements as a function of the annealing temperature. The surface topography of films was investigated by AFM.

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1. Introduction

Chalcogenide as GeSbTe (GST) became a promising material studied for next generation non-volatile memories because of its advantages such as high switch speed, low power consumption, good endurance, high scalability, and fabrication compatibility with complementary metal-oxide semiconductor process. Among different type of memories, phase change random access memory (PcRAM) uses reversible phase change between the crystalline and amorphous states of chalcogenide materials brought about by Joule heating [1]. In present, many efforts have been made to improve the phase change characteristics and device performances. It was found that doping is an effective means of tuning the alloy's phase change properties. A variety of dopants such as O, Ti, Si, Ag, SiO₂ has been used to improve the performances of PCM and PcRAM devices [1- 6].

The nitrogen-doped GST was found also important for improving the performances of PcRAM. When nitrogen is doped into a GST film, it exists in the forms of nitride or N₂ molecules, which could suppress crystalline grain growth [2, 3]. Instead of Ge₂Sb₂Te₅ (GST-225), the chalcogenide type as Ge₁Sb₂Te₄ (GST-124) is used in the present work for nitrogen-doping. However, most studies on the incorporation of nitrogen into GST film have centered on the macroscopic nature of the structural and electrical properties.

In the present work, the amorphous GST-124 thin films were synthesized using high-power impulse magnetron sputtering (HiPIMS). The main advantages of HiPIMS technique is a large increase in the ionization degree of the metallic vapor, since it has been shown that the HiPIMS plasma generates large quantities of highly energetic ions [7] with a directed flux of charged species [8].

2. Experimental set-up

The GST-124 films were deposited by using a magnetron plasma deposition facility with a 3" torus magnetron [9]. The chamber was pumped down to a pressure of 1×10^{-5} Pa before introducing the sputtering gas. Argon and Nitrogen were used as sputtering gas under a total pressure of 0.66 Pa. The films were deposited from a 3" diameter \times 0.2" thick Ge₁Sb₂Te₄ ceramic target (provided by Kurt J. Lesker) onto silicon substrates axially placed in the deposition system. Target to substrate distance was about 8cm and the sputtering was carried out for 30 minutes at 30W.

The target peak power of 10-15 kW was attained during the HiPIMS operation (for – 950 V applied voltage, pulse width of 20 μ s and pulse frequency ranged between 100 and 200 Hz). A 1:100 high voltage probe measured the target voltage.

The as-deposited films were annealed in vacuum at different temperatures between 100-350°C. At the desired temperature the samples were kept for 20 minutes. The heating and cooling ramp was 5°C/min. The base pressure for annealing was 1×10^{-2} Pa. The thickness of the film is 300nm. The amorphous and crystalline phases of GST-124 were measured by X-ray diffraction. The vibrations modes of GST-124 were determined by Raman spectroscopy. The sheet resistance was measured by four-point probe method. The surface topography of films was investigated by atomic force microscopy (AFM).

3. Results and discussions

The XRD analyses established the presence of the amorphous and crystalline phases in the GST-124 coatings. The as-deposited films were growth in amorphous phase in HiPIMS discharge [9].

Figures 1a and 1b show the XRD pattern of 1.8% and 3.7% nitrogen-doped and undoped GST-124 films annealed at temperatures 160°C and 200°C, respectively. It can be seen from figures 1a and 1b that the amorphous state for 1.8% and 3.7% nitrogen-doped GST-124 films is preserved in the temperature range of 160-200°C.

For the same annealing temperature range, the undoped GST-124 films show a mixing between the amorphous and the metastable states face centered cubic (fcc) with diffraction peaks (200) at 29°C, (111) at 26.7° and (220) at 42.8°C, respectively.

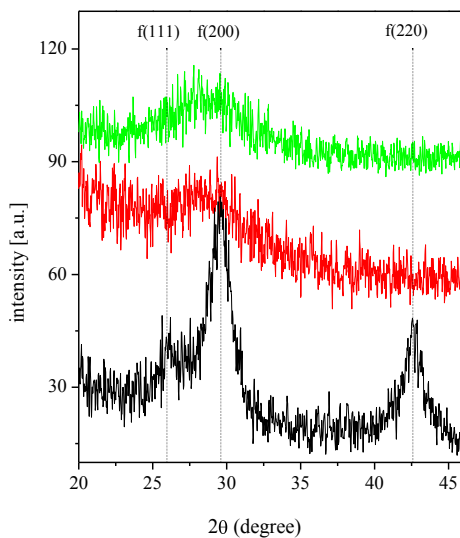


Fig. 1a. The XRD patterns for 1.8% (red curve) and 3.7% nitrogen-doped (green curve) GST-124 and undoped (black curve) GST-124 films. The annealing temperature was 160°C.

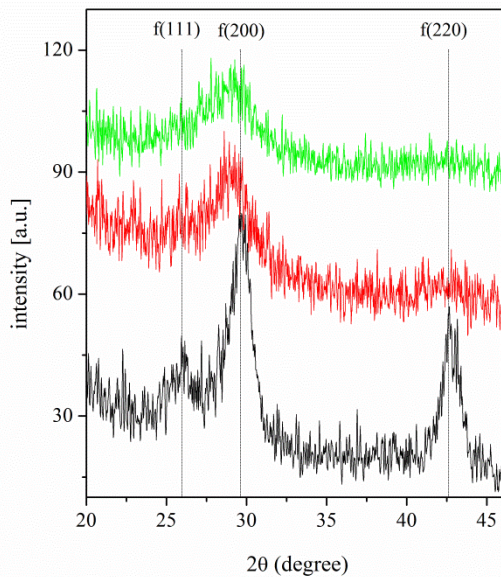


Fig. 1b. The XRD patterns for 1.8% (red curve) and 3.7% nitrogen-doped (green curve) GST-124 and undoped GST-124 (black curve) films. The annealing temperature was 200°C.

An increase in the annealing temperature for 250-350°C, leads to a change in the crystalline structure of films. Figures 2-3 show the XRD pattern for nitrogen-doped and undoped GST-124 films. In this annealing temperature range, the 1.8% and 3.7% nitrogen-doped GST-124 films present a fcc state with diffraction peaks (200) at 29° and (220) at 42.8°, respectively. The undoped GST-124 film presents a stable hexagonal close packed (hcp) state with diffraction peaks (10-3) at 28.6° and (10-6) at 39°, respectively.

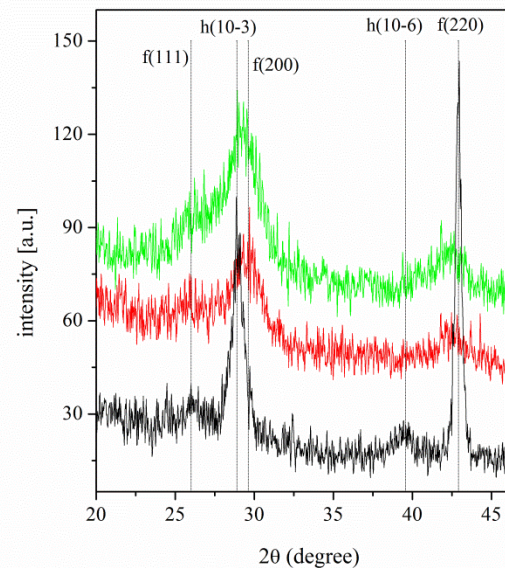


Fig. 2. The XRD patterns for 1.8% (red curve) and 3.7% nitrogen-doped (green curve) GST-124 and undoped (black curve) GST-124 films. The annealing temperature was 250°C.

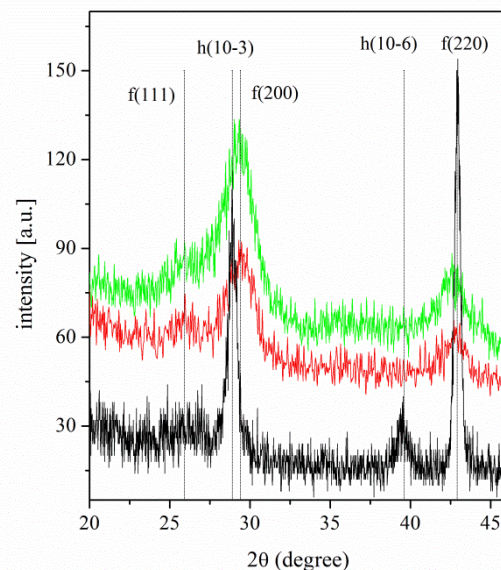


Fig. 3. The XRD patterns for 1.8% (red curve) and 3.7% nitrogen-doped (green curve) GST-124 and undoped (black curve) GST-124 films. The annealing temperature was 350°C.

For the higher amount of nitrogen-doped into GST samples, the measurements of sheet resistance depending on the temperature were performed. The sheet resistance as a function of annealing temperature is presented in Fig. 4.

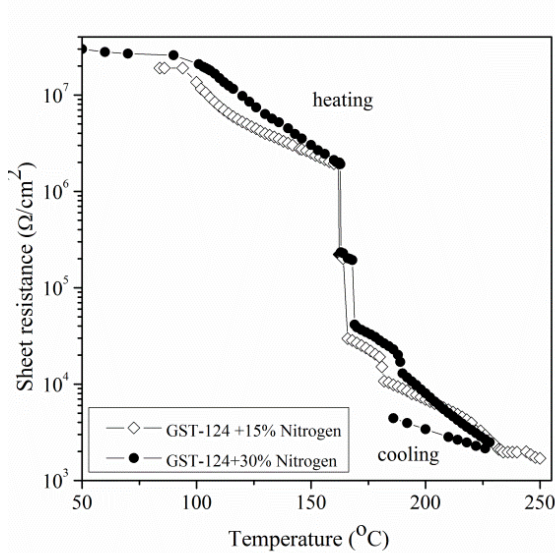


Fig. 4. Plot of sheet resistance as a function of annealing temperature for 15% and 30% nitrogen-doped GST-124 film.

Fig. 4 shows the sheet resistance change of 15% and 30% nitrogen-doped GST-124 films as a function of annealing temperature. From figure 4, two transition temperatures for nitrogen-doped GST-124 film can be seen. A sharp drop at about 160°C was assigned to amorphous-to-fcc transition. A small drop at 180°C for 15% nitrogen-doped GST-124 film and 190°C for 30% nitrogen-doped GST-124 film, respectively, could be attributed to fcc-hcp transition phase. To understand the nature of transitions at 180°C and 190°C respectively, the XRD measurements were performed after the sheet resistance was measured. The XRD measurements presented in figure 5 has been done for the 15% nitrogen-doped GST-124 sample. It can be seen a mixing of the fcc and hcp phases, this mixing could be an indication of hcp transitions for 15% and 30% nitrogen-doped GST-124 film.

A small drop in the sheets resistance at about 165°C may be caused by phase segregation. It was reported for oxygen doped $\text{Ge}_2\text{Sb}_2\text{Te}_5$ a similar behavior of sheet resistance, meaning that for alloys with less excess of Te two transition temperatures are noticed, where the second transition is caused by Te crystallite segregation [10].

For the 15% and 30% nitrogen-doped GST-124 samples, the transition temperature from amorphous-fcc phases was observed at 160°C. Taking into account XRD measurements for 1.8% and 3.7% nitrogen-doped GST-124 samples compared with that of undoped GST-124 sample, an increase of the first amorphous-fcc transition

temperature from 160°C to 250°C could be observed. The first transition temperature amorphous-fcc for nitrogen-doped samples is always presented to 160°C, no matter of the doping amount.

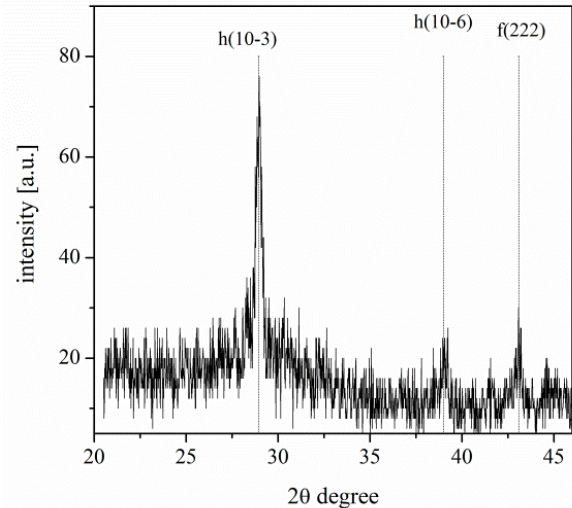


Fig. 5. The XRD patterns for 15% nitrogen-doped GST-124 film presented after sheet resistance measurements. The annealing temperature was 250°C.

When nitrogen is doped into a GST-124 film, even at smaller content, it could exist in the forms of nitride or N_2 molecules, which suppresses the crystalline hcp phase. Nitrogen can form trivalent covalent bonds, which can saturate defects in the amorphous material, increasing the band gap. The presence of more covalent bonds reduces the atomic diffusivity, leading to an increase of the phase change activation energy [2].

Figure 6 shows the Raman spectra for 15% nitrogen-doped GST-124 film at room temperature and heated at 250°C compared with undoped GST-124 film heated at 350°C.

For 15% nitrogen-doped GST-124 at room temperature a broad peak is observed around 140-150 cm^{-1} is regarded as the main feature of the Raman spectrum of amorphous GST, this mode being associated with stretching Te-Te chain [11].

In Raman spectra of undoped GST-124 annealed at 350°C were identified four phonon vibration modes at 66, 121, 140 and 168 cm^{-1} , respectively. The modes at 121 and 140 cm^{-1} could be attributed to the vibration of corner sharing tetrahedral GeTe_{4-n} ($n=0, 1$) and/or pyramidal SbTe_3 . The peak at 168 cm^{-1} can be assigned to Sb-Sb vibration in (Te_2) [12].

For the sample 15% nitrogen-doped GST-124 heated at 250°C, it can be seen three peaks at position 66, 121 and 140 cm^{-1} , respectively. The lack of the phonon mode at position of 168 cm^{-1} could be an indication of nitrides, since the nitrogen atoms are located in the structure and can occupy the vacancies sites. The nitrogen atoms probably exist as Ge-N, Sb-N and Te-N in the film.

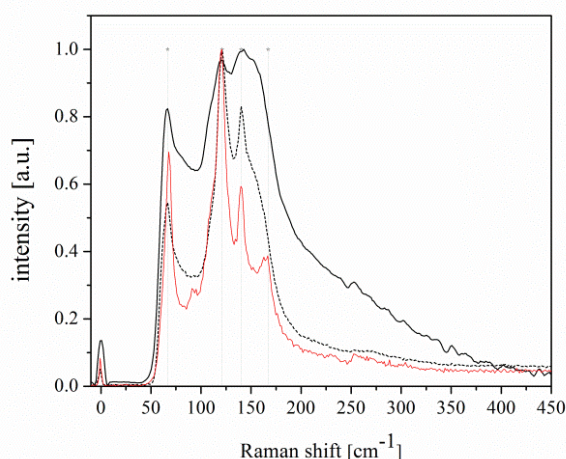


Fig. 6. The Raman spectrum at 514nm for undoped GST-124 sample annealed at 350°C (red curve) and for 15% nitrogen-doped GST-124 sample at room temperature (black curve) and annealed at 250°C (dot black curve), respectively.

The AFM images of the annealed samples at 250°C are shown in Figs 7.

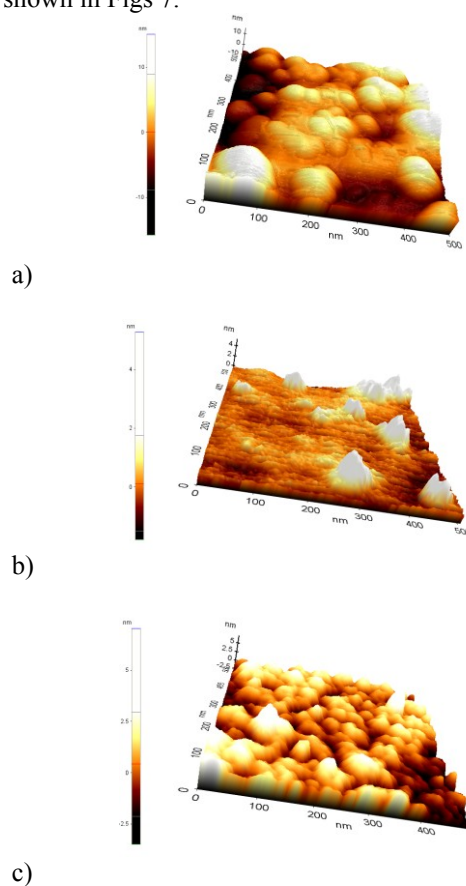


Fig. 7. AFM images a) 3.7% nitrogen-doped GST-124 film; b) 15% nitrogen-doped GST-124 thin film and c) undoped GST-124. The films were annealed at 250 °C.

Film surface roughness is extremely important for device performance, since electrical properties depends not only a well-defined microstructure but also on the quality of the electrode-film interface. The root-mean-square surface roughness of annealed GST-124 thin film at 250°C are 1.264nm, 5.452nm and 0.286nm for nitrogen content of 0%, 3.7% and 15%, respectively. It is an evidence that the surface samples doped nitrogen film is more compact and the grain size became smoother than that of undoped sample.

4. Conclusions

In the present paper, the nitrogen doped-GST-124 and undoped GST-124 films with thickness of 300nm were deposited by high power impulse magnetron sputtering on the silicon substrate. It was found that even at low percentage of nitrogen in the film, the structure of the GST-124 annealed at 350°C is identified as a crystalline fcc phase while for undoped GST-124 the hcp phase is noticed. In the case of higher percentage as 15% and 30% nitrogen-doped GST-124 the transition temperature from amorphous to fcc phase decreased to 160°C close to that for undoped GST-124. Nitrogen doping has a great effect on the resistance annealing behavior of $\text{Ge}_1\text{Sb}_2\text{Te}_4$ film, that origin from the structural changes including suppressing of the phase transition from fcc to hcp. It should to be noted that the inhibition of the crystallization of GST, might offer a large benefit for the stable PcRAM device, because the cell in the amorphous state tend to switch to crystalline state by heat dissipation from other cells. Raman spectra conclude that the lack of vibration mode Sb-Sb in Te_2 observed for nitrogen-doped GST-124 could be an indication of nitrides formation. The AFM topography surface shows a refinement of the grain size in the nitrogen-doped samples.

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