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EFFECT OF TIN ION IMPLANTATION ON THE PROPERTIES OF AMORPHOUS $Ge_2Sb_2Te_5$ THIN FILMS

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Abstract

Alloys along the quasi-binary line between Sb_2Te_3 and GeTe with compositions $(GeTe)_m(Sb_2Te_3)_n$, in particular $Ge_2Sb_2Te_5$, have been intensely studied and are used in the state-of-the-art PCM devices. However, properties of this thin film materials are not optimal and should be improved. In this work, we investigated the effect of tin ion implantation on the properties of amorphous $Ge_2Sb_2Te_5$ thin films. The Sn ion implantation was done on Multipurpose Test Bench (MTB) [1] at NRC "Kurchatov Institute"-ITEP. The MTB consists of MEVVA type ion source, electrostatic focusing system, the system of current and beam profile measurements. The charge spectrum of the Sn beam was measured by the time-of-flight method, the beam profile as well as beam current were also measured. The beam`s accelerating voltage was calculated by SRIM code in order to implant ions on the required film`s depth. Tin ions were implanted into GST films at 40 kV accelerating voltage. Effect of Sn ion implantation (1 at. %) on the electrical properties of magnetron GST thin films was investigated.

INTRODUCTION

Alloys along the quasi-binary line between Sb_2Te_3 and GeTe with compositions $(GeTe)_m(Sb_2Te_3)_n$ (GST) have been intensely studied and are used in the state-of-the-art PCM devices. Doping is the effective method for purposeful change of the properties of GST [2, 3]. In particular, the introduction of tin dopant has a significant impact on the electrical and thermal properties of the bulk Ge-Sb-Te and thin films on their basis [4]. Ion implantation is a doping method, which is very often used for changing the electrical properties of thin films. By choosing appropriate implantation parameters and film thickness uniform Sn distribution along the film thickness and homogeneous properties can be provided. However, implantation process of Sn ion in the GST thin films is not investigated yet. So, the aim of this work is to study the effect of Sn ion implantation (1 at. %) on the electrical properties of magnetron GST thin films.

SAMPLES PREPARING

Thin films of the GST composition were prepared by DC magnetron sputtering at room temperature. The pressure of Ar during the process was $5 \cdot 10^{-3}$ Torr, the sputtering power was 100 W. The amorphous thin films were deposited on the silicon wafers and substrates of thermally oxidized silicon with planar electrodes (TiN/W/TiN). The thicknesses of thin films were controlled by the atomic force microscopy (NT-MDT Solver Pro) and were ~40 nm.

TOF DIAGNOSTICS OF Sn ION BEAM

In order to avoid the surface effects the Sn ions were implanted on the middle of the film thickness. The implantation depth was determined by acceleration voltage as well as by charge state beam. The Time-of-Flight method was used to determine the beam charge state of MEVVA ion source with Sn cathode [5]. The 5 peaks were observed at the output of TOF channel: T1 – 48 μs, T2 – 33 μs, T3 – 22.5 μs, T4 – 17 μs, T5 – 14 μs. The peaks T1 and T2 corresponds to Sn^+ and Sn^{2+}, while T3-T5 to residual gas and hydrocarbons. The total amount of Sn ions consists of 43% Sn^+ ions and 57% Sn^{2+}.

THE ACCELERATING VOLTAGE OF Sn ION BEAM

In order to make Sn ions Bragg peak position at the GST225 film required depth the accelerating voltage was determined by SRIM code. The simulation has shown that Sn ions Bragg peak is located at 20-25 nm depth at 40 kV accelerating voltage (see Fig. 1).

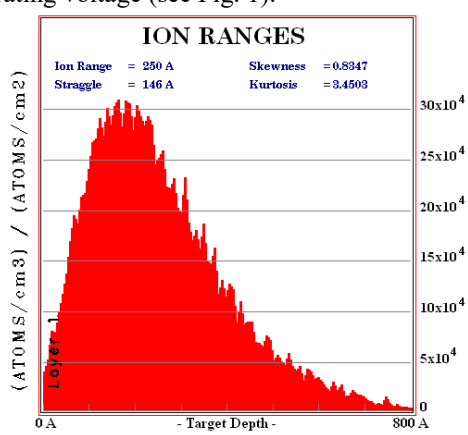

Figure 1: The Bragg peak of Sn ions (Sn^+ and Sn^{2+}) in the GST225 film at 40 kV accelerating voltage.

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THE BEAM PROFILE AND CURRENT MEASUREMENTS

The Sn beam profile was measured at the 250 mm distance from the ion source. The profilometer consists of the number of 70 mm long wires with 1 mm diameter and located at 1 mm to each other. The beam profile at the horizontal plane is shown on Fig. 2, where green lines show the target area. The beam irregularity at the target position is ±10%. The vertical beam profile is the same as at the horizontal plane.

The beam current was measured. The beam pulse length was 250 μs. Calculated fluence was equal to $9{,}68 \cdot 10^{10}$ p/cm^2.

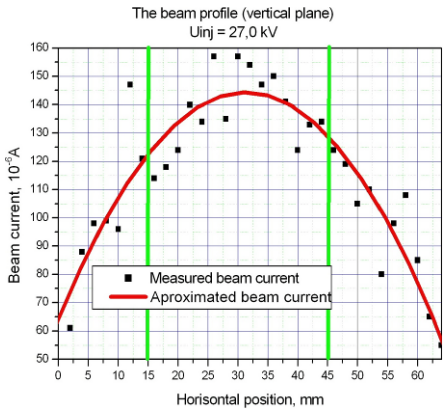

Figure 2: The beam`s profile.

THE Sn IONS IMPLANTATION INTO THE GST225 FILM

The profilometer was replaced by the combined target which consists of the target, suppressor and defending rings (see Fig. 3). The last two rings were required to avoid secondary electron emission. The target with the GST225 samples was located at the profilometer plane. The -500 V potential was applied to the suppressor ring, defending ring at zero potential while target was a current collector. The Sn ions implantation was carried out at 40 kV accelerating voltage, pulse time of 250 μs, repetition rate of 1 Hz, vacuum of $6 \cdot 10^{-6}$ mbar.

The total number of pulses was 1430, which corresponds to the fluence $1{,}3845 \cdot 10^{14}$ p/cm^2, and provides Sn concentration in GST225 film of 1 at. %.

THE SAMPLES INVESTIGATION AFTER IONS IMPLANTATION

The uniformity of the element distributions across the film thicknesses was determined by Time-of-Flight secondary ion mass (Ion TOF ToF.SIMS 5) and Auger electron (Physical Electronics PHI-670xi) spectrometries (see Fig. 4). The main ionic fragments of Ge, Sb, and Te are distributed evenly in the volume of the film. The Sn profile of the amorphous thin films has a distribution characteristic of ion implantation with a maximum near 20 nm. It should be noted, that a natural oxide was formed in the near-surface layer of the films, which contributes to the change of the output coefficients for the ionic fragments. As a result the secondary ion current of the elements changes, which manifests itself in the form of the peaks near the surface/film interface (~ 5 nm).

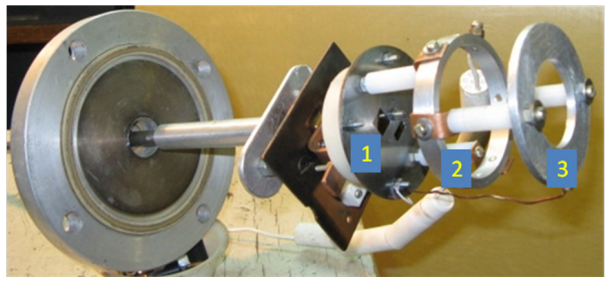

Figure 3: Combined target where 1 – target, 2 – suppressor ring, 3 – defending ring.

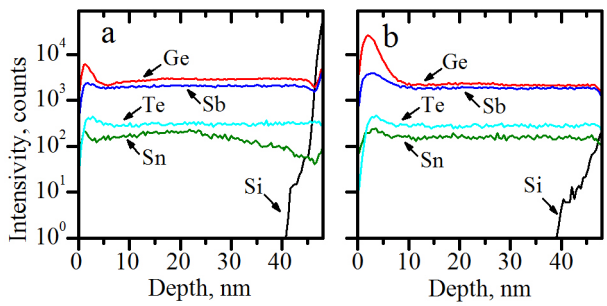

Figure 4: Elemental distributions along the film thicknesses according to TOF-SIMS for Sn-doped GST225 thin films: a – before annealing; b – after annealing at 400 °C.

Figure 4 shows the experimental distribution of Sn ions implanted into amorphous (a) and crystalline (b) GST225 thin films. One can see that at elevated temperature the diffusion of the implanted atoms leads to a broadening of the profile. Heat treatment (HFS600E-PB4 Linkam) up to 400 °C with the heating rate of 1 °C/min in the Ar atmosphere leads to smoothing of the Sn distributions profile in the thin films.

On Figure 5 one can find the temperature dependencies of resistivities for undoped and Sn-doped GST225 samples. Results of the analysis of the obtained temperature dependencies are presented in Table 1, where T_{set} and T_{end} are onset and endset temperatures of crystallization, ρ_{set} and ρ_{end} are resistivities for amorphous and crystalline states, E_a is the activation energy of conductivity.

The exponential dependencies of the electrical conductivity for amorphous films in the range from room temperature to 150° C were observed, and electrical conductivity activation energies were calculated. The implantation of Sn ions in the GST225 thin films does not have an effect on the Ea, but leads to a significant decrease in the resistivity of the amorphous thin films.

Also, the implantation of Sn ions in the GST225 thin films leads to the decrease of the crystallization temperatures, which potentially can be used for decreasing a writing power of the PCM cell.

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The Raman spectra of the GST225 and Sn-doped GST samples were obtained by Horiba LabRAM HR Evolution. The He-Ne laser (633 nm, 10 mW) was used as a source of excitation radiation. The maximums near 150 and 100 cm^{-1} were chosen for the normalization of the Raman spectra of samples before and after annealing at 400 °C, respectively (Fig. 6).

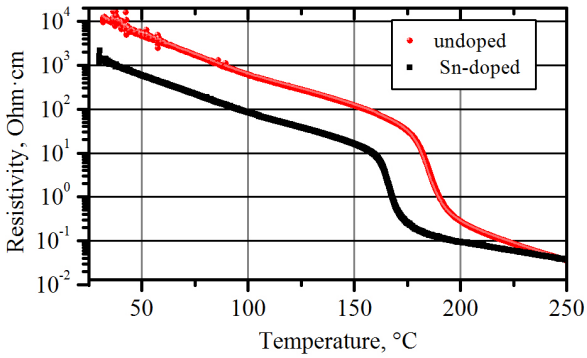

Figure 5: Resistivity temperature dependencies for investigated films.

Table 1. Electrical Properties of Investigated Thin Films

T_{set}, °C	T_{end}, °C	ρ_{set}, Ω·cm	ρ_{end}, Ω·cm	E_a, eV
undoped GST thin film				
176,7	193.9	$4.58 \cdot 10^3$	$5.11 \cdot 10^{-1}$	0.43
Sn-doped GST thin film				
161.1	173.1	$5.80 \cdot 10^2$	$3.23 \cdot 10^{-1}$	0.42

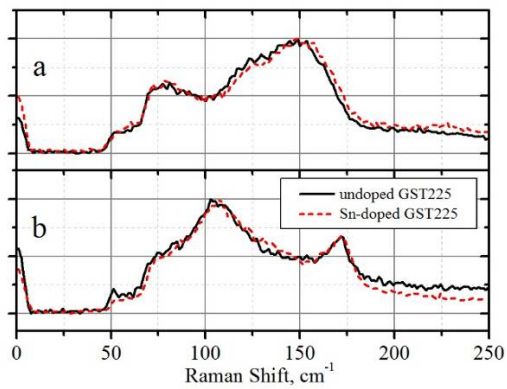

Figure 6: The normalized Raman scattering spectra for undoped and Sn-doped GST225 thin films: a – before annealing; b – after annealing at 400 °C.

Analysis of the Raman data showed that five main peaks for amorphous thin films could be determined. Positions of this peaks (56, 75, 121, 151 and 212 cm^{-1}) are characteristic for the amorphous $Ge_2Sb_2Te_5$ films [6]. The thermal annealing (400 °C) is accompanied by the changes of the Raman spectra shape. The positions of the decomposed peaks are close to the peak positions for GST thin films with hexagonal structure.

It should be noted, that shapes of the normalized spectra for undoped and Sn-doped thin films are close. So, the influence of the Sn incorporation by implantation method on the structural units of GST225 thin films was not observed. This result can be due to the effective replacement of the germanium by tin or to the introduction of tin ions into defects of the vacancy type.

Thus, we observed the electrical activity of the tin impurity atoms typical for the chalcogenide semiconductors, which is possible if there is no structural relaxation of the structure. Such behavior was repeatedly observed during the implantation of ions into vitreous chalcogenide semiconductors and Ovshinsky called this method a chemical modification of the amorphous chalcogenide semiconductor films. As a rule, in this case the activation energy practically does not change in the case of intrinsic conductivity, and the changes can be noticed only for the impurity conduction. However, we did not see impurity conduction at these in the measuring temperature range (in order to see it we must use much lower temperatures).

CONCLUSION

So, obtained results showed that tin ion implantation changes the electrical properties of the amorphous GST225 films and their crystallization temperatures, which can be used for the optimization of the parameters of the PCM layers.

ACKNOWLEDGEMENTS

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