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A COMPARATIVE STUDY OF $GeSb_2Te_4$ FILMS DEPOSITED BY RADIOFREQUENCY AND PULSED DIRECT-CURRENT AND MAGNETRON SPUTTERING HIGH POWER IMPULSE MAGNETRON SPUTTERING

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The phase change memory (PCM) is a rather new and promising procedure, which proposed the chalcogenide compound to be used as active material because it satisfies various criteria needed for non-volatile memory devices. The $Ge_1Sb_2Te_4$ compounds represent good candidate for PCM devices because they have a rapid switching speed and are suitable in semiconductor fabrications. Amorphous $Ge_1Sb_2Te_4$ thin films were deposited on silicon substrates using high power impulse magnetron sputtering, RF magneron sputtering and pulsed DC magnetron sputtering. The X-ray diffraction patterns of as-deposited and annealed films present crystallization from amorphous to face cubic centered and further to hexagonal phase. A similar crystalline structure was observed for film obtained by high power impulse magnetron sputtering and RF magneron sputtering while those obtained by pulsed DC magnetron sputtering presented an unexpected variation of structure with temperature. The surface of the as-deposited and annealed films was investigated by AFM. It was found an increasing of the annealed film roughness at transition from face cubic centered to hexagonal closepacked phases. The Secondary Ion Mass Spectrometry results confirm a longer depth profile of Te element in the annealed film sample, deposited by high power impulse magnetron sputtering, than those obtained by conventional techniques.

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Keywords: Chalcogenide, HiPIMS, Thin film

1. Introduction

Chalcogenide materials are becoming one of the most studied classes for storage media with application in rewritable optical and non-volatile electronic memories. Among different type of memories, phase change memory (PCM) is a technology for the next generation non-volatile memories. The storage mechanism of PCM is based on the change of electrical resistance due to a reversible structural transition between amorphous (high resistance) and crystalline (low resistance). The development of phase change random access memory (PCRAM) technology is very actively by several companies around the world. It is a very promising new non-volatile memory technology. PCRAM technology is based on the difference between the resistivity of phase change materials in the amorphous and crystalline phase (three to five orders of magnitude is typical), and the repeatable and fast switching of the materials between these two phases. The transition from the amorphous to the crystalline phase is induced by heating the material above its crystallization temperature for a long enough time, and the switching back to the amorphous phase

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is realized by melting and quenching the material fast enough that it solidifies in the amorphous state [1-4].

The most commonly used and most studied PCM is $Ge_2Sb_2Te_5$. One peculiarity of $Ge_2Sb_2Te_5$ and other materials on the pseudobinary GeTe-Sb_2Te_3 line such as $Ge_1Sb_2Te_4$ or $Ge_1Sb_4Te_7$ is that they crystallize upon heating, first into a metastable rocksalt structure and then at higher temperatures into a stable hexagonal phase [5].

In the present work, amorphous $Ge_1Sb_2Te_4$ (GST-124) thin films were synthesized using high-power impulsed magnetron sputtering (HiPIMS) and their properties were analysed and compared with those of samples obtained by conventional techniques such as radiofrequency magnetron sputtering (RFMS) and pulsed direct-current magnetron sputtering (PDCMS), respectively. The main advantages HiPIMS technique is a large increase in the ionization degree of the metallic vapor, where it has been shown that the HiPIMS plasma generates large quantities of highly energetic ions [6] with a directed flux of charged species [7]. The lower deposition rate for HiPIMS compared with conventional techniques (RFMS and PDCMS) for the same average power is often reported as a drawback, and is one of the most discussed topics in this field of research [8-12]. The field of ionized physical vapor deposition (IPVD) through high power impulse magnetron sputtering (HiPIMS) is continuously expanding, this being a promising technique for improving the common magnetron sputtering used in many industrial processes for thin film deposition [8].

2. Experimental

The GST-124 films were deposited by using a magnetron plasma deposition facility with a 3" torus magnetron (provided by Kurt J. Lesker). The same magnetron gun was powered in RFMS, PDCMS and HiPIMS mode using a Huettinger PFG 300 RF-generator, a Pinnacle Plus+ DC power supply and a high power pulse generator, respectively. The chamber was pumped down to a pressure of 1×10^{-5} Pa before introducing the sputtering gas. Argon (99.99% purity) was used as sputtering gas under a total pressure of 0.66 Pa. The films were deposited from a 3" diameter × 0.2" thick $Ge_1Sb_2Te_4$ ceramic target (provided by Kurt J. Lesker) onto silicon substrates axially placed in the deposition system. Target to substrate distance was about 8 cm and the sputtering was carried out for 15 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 μs and pulse frequency ranged between 100 and 200 Hz). A 1:100 high voltage probe measured the target voltage. The voltage target and the current target are presented in the figure 1.

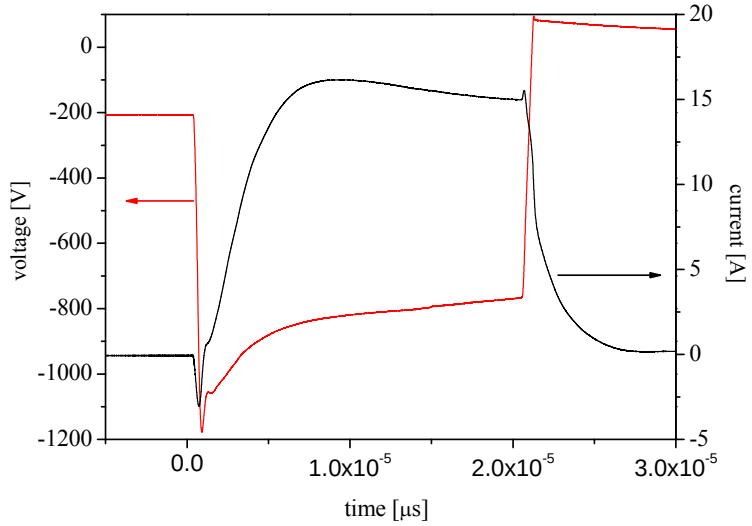


Fig. 1. Typical shape of the HiPIMS current and voltage during a discharge pulse.

The X-ray diffraction (XRD) scans were performed using a Shimadzu model 6000 diffractometer, operating at a wavelength of 1.5418A (Cu Kα radiation, 40 kV, 30 mA), under the grazing incidence angle (θ) of 1 degree and 2θ of 20-50 degrees. The surface topography of as-deposited and annealed films was investigated by atomic force microscopy (AFM) in non-contact operating mode using a Park XE-100 equipment (silicon tip with conical shape). The Hiden Analytical SIMS workstation working with Ar ions at pressure of $3x10^{-5}$Pa was used to obtain the cross section elemental composition of GST-124 thin films. The spot dimension of ion beam is 100 μm, the depth resolution 5nm and the base pressure is 10^{-6}Pa.

The $Ge_1Sb_2Te_4$ thin films were prepared on Si substrates by RFMS, PDCMS and HiPIMS, respectively. The as-deposited films were isothermal annealed in vacuum at different temperatures between 160-400^{o}C, each sample was annealed for 20 minutes at base pressure of $1.33x10^{-4}$Pa. The film thickness was measured using by AFM using a small mask step. The thickness of the film are around 300nm.

3. Results and discussions

The XRD analyses established the presence of the amorphous and crystalline phases in the coatings. The as-deposited films were growth in amorphous states in all type magnetron sputtering discharges, as one can see in the figure 2.

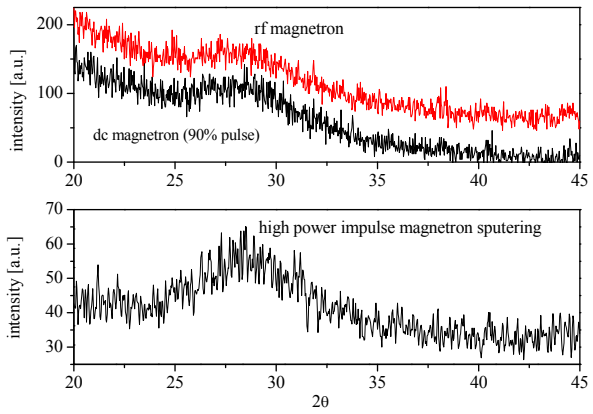
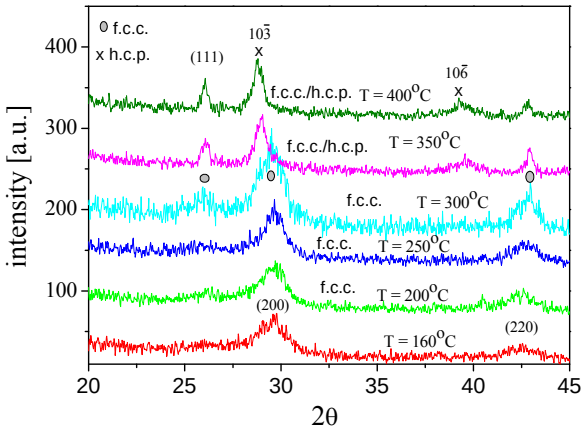


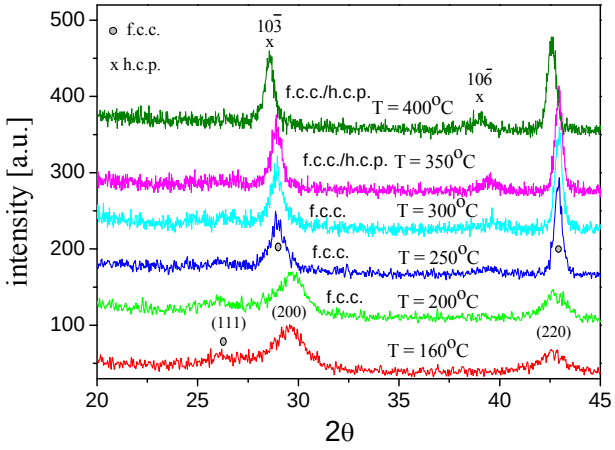
Fig. 2. The X-ray diffraction pattern for as-deposited GST-124 thin film. The average power in all sputtering discharges is P = 30Watt. The broad peak at 27^{o} indicated the amorphous phase of $Ge_1Sb_2Te_4$.

Figure 2 shows a broad peaks near 27° for amorphous phase instead of sharp X-ray diffraction peaks.

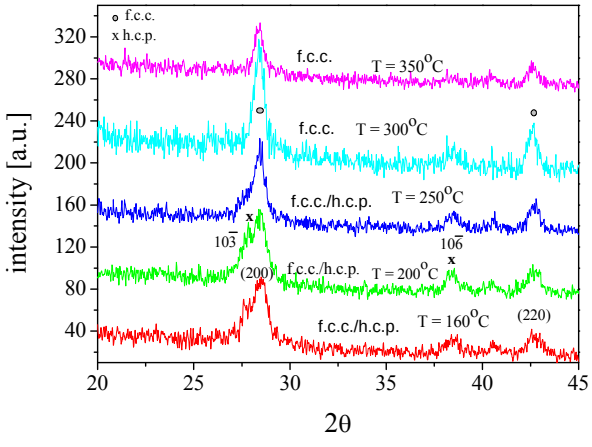
Figures 3 present the X-ray diffraction patterns for annealed GST-124 films.



3a



3b



3c

Fig. 3. The X-ray diffraction patterns of annealed films at different temperatures, deposited at P=30W using: a) RFMS, b) HiPIMS and c) PDCMS.

In the temperature range of 160-250°C, the GST-124 films show a metastable phase, face cubic centered (f.c.c.) and a minor amorphous phase, as shown in Figures 3 where a broad and weak peak originating between 26° and 29° is present. In addition, for samples growths in RFMS

and HiPIMS, we can notice from figures 3a- b a mixing between the metastable state (f.c.c.) and transition to stable hexagonal closepacked state (h.c.p.) of GST-124 films in the temperature range of 250-400^{o}C. The metastable state structure of GST-124 has two main diffraction peaks of (2,0,0) at 29^{o} and (2,2,0) at 42.8^{o} with a small peak (1,1,1) at 26.7^{o}.
The hexagonal closepacked state presents two small diffraction peaks of (1,0,-6) at 39^{o} and (1,0,-3) at 28.5^{o}.

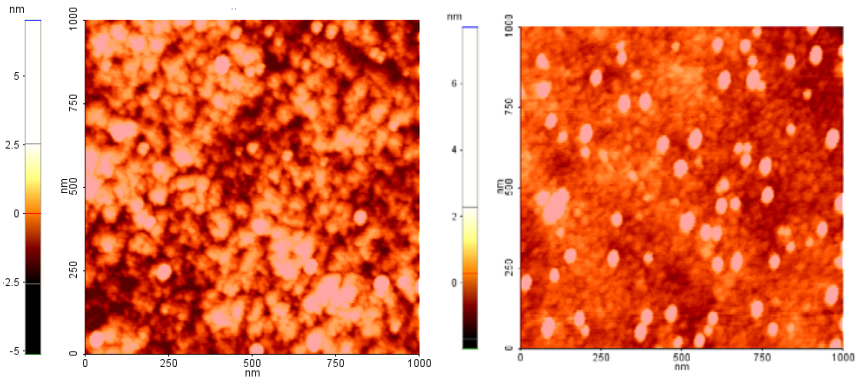
By our X-ray diffraction measurements the transition temperature to fcc metastable state and to hcp state are approximate 200^{o}C, and 300^{o}C, respectively.

Compared to films growth in RFMS and HiPIMS, the PDCMS film during annealing shows an unexpected behaviour, the hexagonal closepacked phase mixed with face cubic centered phase at low annealing temperatures of 160-200^{o}C is present. Diffraction peaks coresponding to hcp state appear at (1,0,-6) at 39^{o} and (1,0,-3) at 28.5^{o}, as one can see from figure 2c.

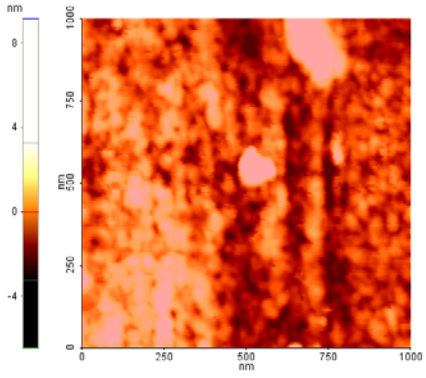
The AFM images of the annealed samples are shown in figures 4a-c. The crystallization of the material surface samples close to fcc/hcp transition phases leads to an appreciable increase of the roughness. The as-deposited and annealed films had relatively uniform surfaces but at high temperature many crystallites had grown on the surface films, the crystallites grains increased as the annealing temperature is increasing. At higher temperatures, around 400^{o}C, the surface of the films exfoliated, this temperature could be estimated as the superior limit for application. The roughness of as-deposited and annealed films are presented in table 1. The AFM images show a uniform and compact surface for films growth in HiPIMS than those growths in conventional techniques.

Table 1. The roughness of the as-deposited and annealed GST-124 films. The annealed temperature is 250^{o}C.

Roughness	RFMS	PDCMS	HiPIMS
as-deposited	1.013nm	0.542nm	1.253nm
T =250^{o}C	1.039nm	1.672nm	1.367nm



4a 4b



4c.

Fig 4. The AFM image of the GST-124 film annealed at T = 250^{o}C and deposited using: a) HiPIMS, b) RFMS and c) PDCMS.

The secondary ion mass spectrometry (SIMS) depth profiles of substrates and Te are shown in figure 5, for GST-124 films growth in all sputtering discharges and annealed at T = 350°C.

As reported in the literature, in the $Ge_2Sb_2Te_5$ (GST-225) films during annealing, the Te with low melting temperature is most likely to migrate in the layer to the sample surface [13,14]. From figure 5 it can be observed that Te signal of sample deposited in HiPIMS has a longer depth profile than those of samples deposited by conventional techniques, even the deposition parameters are kept constant in all discharges. One of the main advantages of HiPIMS technique is a large increase in the ionization degree of target elements, so that the HiPIMS plasma generates large quantities of highly energetic ions. Therefore, increasing the ionization of the sputtered vapor gives an improvement of the film quality, such as density, higher hardness, improved surface roughness, control of the reactivity [15-19].

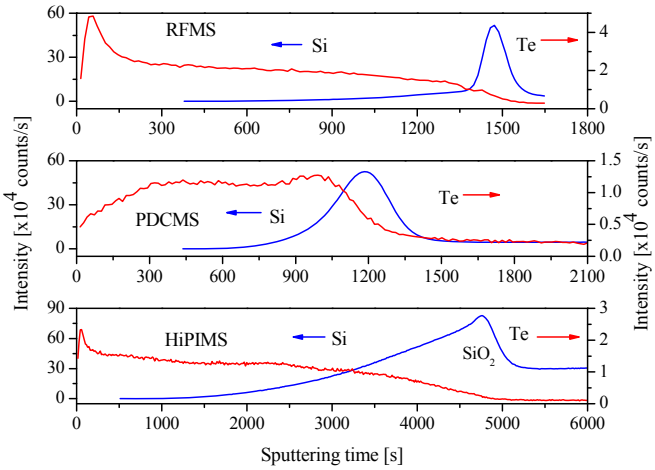


Fig. 5. SIMS profiles for Si substrate and Te atom of GST-124. The films were annealed at T = 350°C and deposited using: a) RFMS, b) PDCMS and c) HiPIMS. The peak in the SIMS profile of Si is silicon oxide at the substrate surface.

4. Conclusion

In summary, we made a comparison between the three sputtering types from the point of view for technical applications of chalcogenide material target. It was shown by X-ray diffraction that GST-124 film is grown in amorphous phase in all sputtering discharges, and during annealing films growth by RFMS and HiPIMS are quite similar, an unexpected behaviour was noticed for the film obtained by PDCMS.

The AFM surface topography of deposited samples by all discharges have relatively uniform surface. The roughness of films increased with the annealing temperature close to hexagonal structure. A higher roughness is observed for PDCMS deposited samples annealed to 250°C since at this temperature the film has hexagonal phase.

Particularly, by SIMS measurements a lower migration of Te to annealed layer is observed for the film grown in HiPIMS than in conventional RFMS and PDCMS, respectively. The deficiency of Te atoms in the film layer leads to PCM cell failure during the thermal device cycling. By our SIMS measurements on the depth profile GST-124 atoms, we conclude that HiPIMS is a good deposition technique regarded the conventional methods as RFMS and PDCMS, respectively. Therefore, HiPIMS is a high promising discharge that could be successfully used not only for pure metallic target but also for more complex material target such as chalcogenide based on GST system.

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