Pressure effects on the growth of Sb_2Te_3 thin films processed by DC and RF sputtering

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Abstract

In this work, are compare and analyze the surface structure, morphology and electrical properties of antimony telluride (Sb_2Te_3) thin films grown by Direct Current (DC) and Radio Frequency (RF) magnetron sputtering system, with the variation of deposit pressure (P_d) from 5 to 15 mTorr. The Sb_2Te_3 thin films were grown with a magnetron power of 60 W, a substrate temperature of 200 °C and deposited time of 60 minutes for all samples. Profilometry measurements, X-ray Diffraction (XRD), morphology by Scanning Electron Microscope (SEM), Energy Dispersive Spectrometry (EDS) and resistivity were carried out on the Sb_2Te_3 thin films. XRD results show that the Sb_2Te_3 thin films prepared by DC sputtering system have a higher crystalline quality respect to thin films deposited by RF sputtering and the structural properties improved by the decreasing of the deposition pressure. Morphology results revealed that when the work pressure in both sputtering systems decreased to 5 mTorr, the grains are more compacted. EDS analyses show that the atomic composition is approximately 35% at of Te and 65% at of Sb in both sputtering systems. Finally, for DC sputtering or RF sputtering systems the resistivity of the thin films decreases is close to $5.8x10^{-4}$ ohm-cm.

1. Introduction

The study of the physical properties of materials deposited by different sputtering techniques is today a field of opportunity to improve the thermoelectric performance. In this publication, we put special interest in the compound Sb2Te3 because its applications are well known in the improvements in the redesign and fabrication of thermoelectric devices, temperature sensors and solar cells. It is important to mention that besides being considered a low cost material and can be substitute materials that have typically increased their cost in the industrial market.

Due to its physical property, such as thermoelectric effect, the Sb_2Te_3 is of great interest for development thermoelectric devices, temperature sensors and solar cells. If Sb_2Te_3 is alloyed with other V-VI compounds, thermoelectric materials can be fabricated. Recently, Sb_2Te_3 has been shown to be a topological insulators depending of level doping (exhibit insulator-like properties within the bulk, and metal-like properties on the surface). If carrier concentration, doping, crystallinity or another property can be modified then the Sb_2Te_3 change its behavior; for example, Sb_2Te_3 shows a crystalline–amorphous phase transition at a temperature of around 140°C (1). For solar cells application in the thin film technology CdS/CdTe, Sb_2Te_3 thin films are using like back contact and the sputtering deposition technique might be an important factor with respect to the good performance of this kind of solar cells (2,3).

Sb_2Te_3 thin films have been obtained by several growth systems, e.g., MOCVD (4–6), electrochemical deposition co-evaporation (7–9), and sputtering (10). Noteworthy progress has recently been made regarding the atomic layer deposition (ALD) of Sb_2Te_3 thin films, offering the possibility to create highly defined thin layers (10 nm + number of monolayer's) of ideal stoichiometry and Sb_2Te_3 with a low defect concentration. The properties of Sb_2Te_3 deposited by Co-sputtering have optimized as a function of several experimental parameters like magnetron power, substrate temperature and time deposition; in general, the typical case of study is the effect of substrate temperature over the morphology (11,12). However, not many papers go beyond structural, morphology and electrical characterization of Sb_2Te_3 thin films grown by DC and RF magnetron sputtering, with the variation of deposition pressure. In this work we discuss these properties of Sb_2Te_3 thin films deposited by DC and RF sputtering system.

2. Materials and equipment

Experimental Description of the Sb_2Te_2 thin films growth

For both DC and RF Sb_2Te_3 thin films, commercial soda lime glass (SLG) and glass/SnO_2:F Tec15 Pilkington were used as substrate. The substrates were cleaned using alkaline biodegradable liquid soap in deionized water prior to a 10 min isopropyl alcohol solution in an ultrasonic bath and dried with nitrogen. The diameter of Sb_2Te_3 target was 75.3 mm with a purity of 99.999%. The glass substrates rotated at 5 rpm during the growth to enhance the uniformity of the deposited films. The base pressure in the chamber was $8x10^{-6}$ Torr, the sputtering process was carried out at a constant power of 60 W and varying the pressure from 5 to 15 mTorr, using pure Ar as the working gas for both sputtering systems. The temperature of the substrate was maintained constant at 200°C with a source power Sorense during a deposit time of 60 min in both sputtering systems. Similarly, an Inficon SQM-160 instrument monitored the layer thickness during the deposit and the distance between magnetrons (Kurk Lesker type), the substrate was of 100 mm. For DC Sputtering system was used a source power supply Mag Technology, while for RF Sputtering system the source power Kurk Lesker R301 model was used.

Continuing with the process, target surface cleaned by pre-sputtering for 5 min at 60 W of power under pure Ar gas, while the substrate covered with a shutter. Once the preparation and cleaning of the target were finished, the deposition film process started. The flow rate of Ar varied through the mass flow controller from 4 to 23 sccm (standard cubic centimeter per minute) into the chamber to obtain the working pressure between 5 to 15 mTorr in both sputtering systems. The deposition rate was around of 0.4 – 2.1 A/s and it depends on the different values pressure used in the two sputtering systems.

Description of measurement and characterization of the Sb_2Te_2 thin films

A step profiler (Sloan Dektak II) was used to verify the thickness and the roughness obtained. Crystalline structure was determined by the X-ray diffraction patterns (XRD), by means of a D8 Bruker X-ray system using the CuK_α line. Morphological analysis was made using a SEM and the composition of the films on glass substrates was obtained by EDS studies with a JEOL JSM-6701 model microscope with an acceleration voltage of 5 kV, allowing a resolution of 2 nm with an Oxford Instrument Energy 200 EDS analytical system. The resistivity of the Sb_2Te_3 thin films was measured using a four-probe method.

3. Methodology

According to the scientific literature, the electrical properties as a function of the variation of the substrate temperature were compared in this work (12), with good results in correlation.
Two sets of samples were designed, one for DC sputtering and other for RF sputtering systems. The experiments for RF-Sp (RF Sputtering system) were set up three samples varying deposition pressure (RF1-10, RF2-15 and RF3-5 mTorr) and the experiments for DC-Sp (DC Sputtering system) were set up three samples varying deposit pressure too (DC1-10, DC2-15 and DC3-5 mTorr). The input power source of 60 W and substrate temperature of 200 °C remain constant in each of the two sputtering systems, this temperature it's is closed to temperature reported in Tianbao Chen, et al. where mention Sb_2Te_3 samples more stoichiometric at this temperature. Table I shows the experimental parameters used in this work.

Table I. Experimental parameters used for the Sb_2Te_3 thin films growth

Sputtering-System	DC – Sp			RF – Sp		
Sample name	DC3	DC1	DC2	RF3	RF1	RF2
P_d (mTorr)	5	10	15	5	10	15
T_{sub} (ºC)	200					
Power (W)	60					

4. Experimental Results

Profile measurements

Figure 1 shows the results of samples in the DC-Sp system. When the chamber pressure is increased from 5 to 15 mTorr, the layer thickness decreases as well as the grown rate that went from 13 to 2.6 nm/min. On the other hand, the roughness increase from 22 to 32 nm was observed when the deposit pressure increases in the same range. For the RF-Sp samples, we can see a similar behavior with respect to the DC-Sp samples and the grown rate varies from 8.8 to 2.5 nm/min.

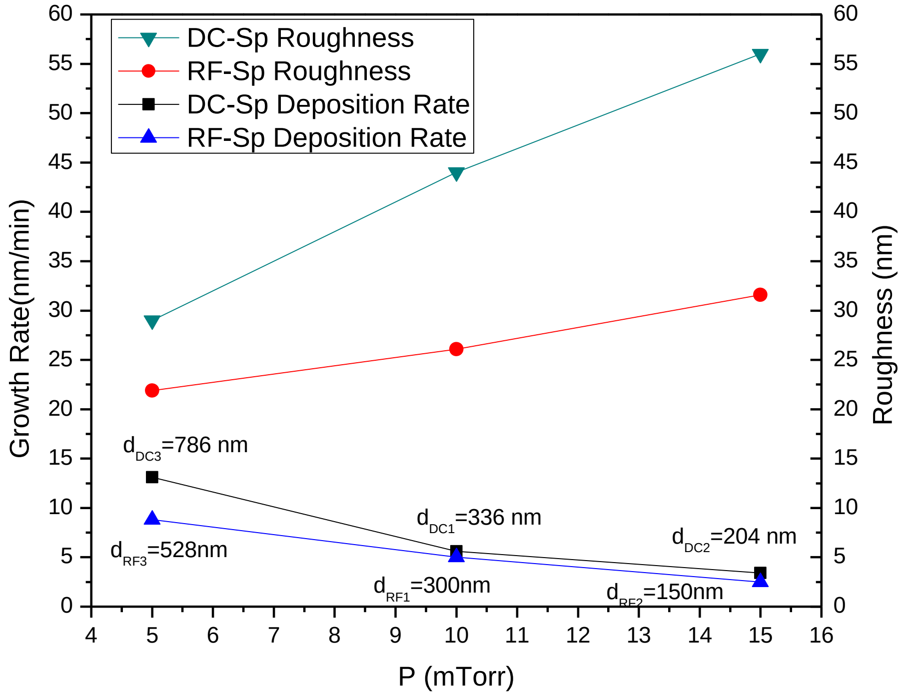


Figure 1. Thickness, roughness and growth rate for Sb_2Te_3 thin films deposited by DC and RF Sputtering system as a function of deposition pressure.

XRD results

Figure 2 and 3 show the XRD patterns for Sb_2Te_3 samples prepared in DC-Sp and RF systems, respectively. Samples deposited by DC-Sp system from 5 to 15 mTorr are polycrystalline with high crystalline quality being that sharp and well-defined peaks are observed from the patters. The comparison of the diffraction lines with PDF files (PDF 03-065-3678 and 01-089-6185) indicates that the films crystallize in rhombohedral structure. However, the film deposited at 5 mTorr displays a small peak of monoclinic Sb_2Te_3 crystalline phase (PDF 01-080-8016) and also exhibits preferential orientation to (01<u>14</u>) plane as the intensity of this reflection is higher than that reported for powders. As deposition pressure increases, small reflexions become flat indicating that the preferential orientation on (01<u>14</u>) plane is extinguished and orientation in (015) plane predominates. The bibliography reports Sb_2Te_3 films deposited by thermal co-evaporation with strong preferential orientation on (01<u>14</u>) family planes (13). On the other hand, a similar behavior for XRD results we observe for Sb_2Te_3 thin films deposited on flexible polyimide substrates by DC-Sp (14).

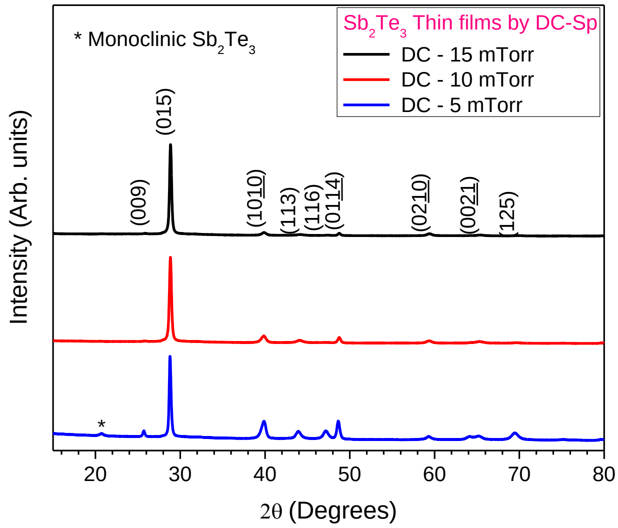


Figure 2. XRD patterns of Sb_2Te_3 thin films deposited by DC-Sp at different pressure.

The patterns of the films deposited by RF-Sp system (Figure 3) have a strong contribution from the amorphous substrate (2q=15-40°) which increases for thinner films. All films show diffractions peaks corresponding to rhombohedral structure. The decrease of deposition pressure promotes higher crystalline quality into the RF sputtering films and preferential orientation on (01<u>14</u>) plane. Besides, films deposited at 10 and 15 mTorr present small reflections, around 15.7, 20.9 and 24.7 degrees, assigned to monoclinic structure of Sb_2Te_3.

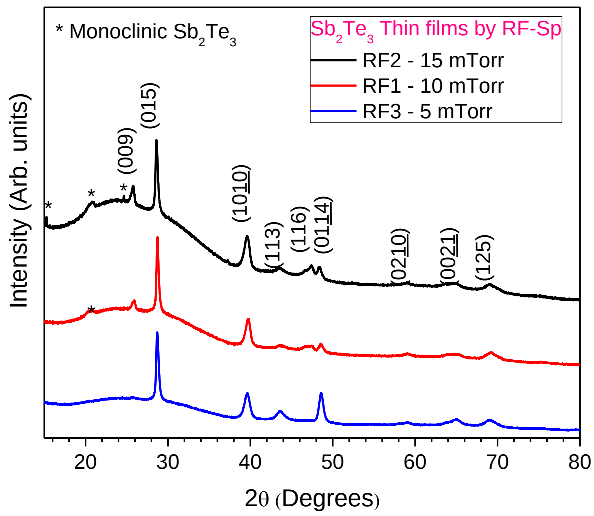
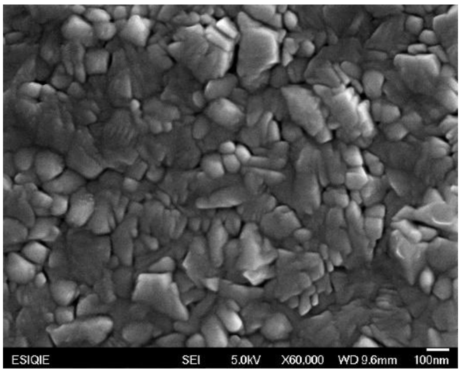


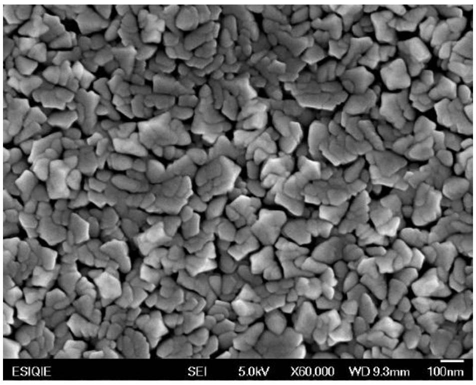
Figure 3. XRD patterns of Sb_2Te_3 thin films deposited by RF-Sp at different pressure.

Morphology

In figure 4, we show the morphology of the DC-Sp samples as a function of deposition pressure. When the work pressure increases for Sb_2Te_3 thin films, the grains are less compact and the grain size increases irregularly from 100 nm to 300 nm approximately in disorder orientation. An opposite effect it was observed when the substrates are flexible polyimide, where at low deposit pressures promote the growth of Sb_2Te_3 by DC-Sp in a polydirectional way and fast accumulation of the micro-flakes, leading to a diversity in the sizes of flakes (14).



a)



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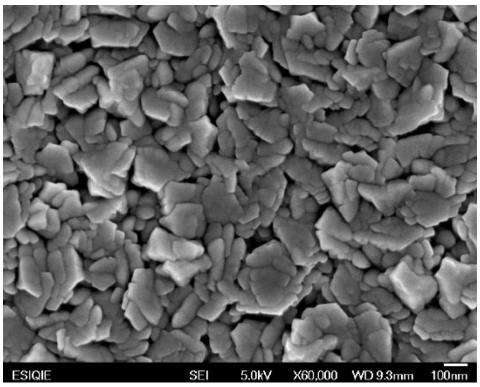
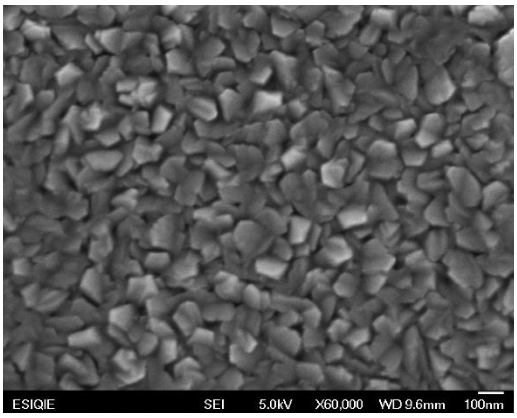


c)

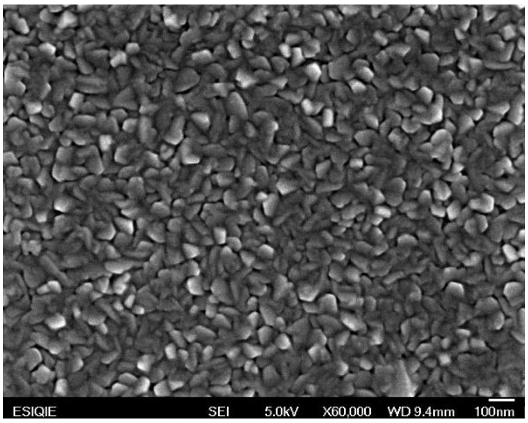
Figure 4. Morphology images for Sb_2Te_3 by DC-Sp as a function of deposition pressure: a) 5 mTorr, b) 10 mTorr and c) 15 mTorr.

In figure 5, we observed the morphology of the Sb_2Te_3 RF-Sp samples as a function of deposition pressure. The grain size of Sb_2Te_3 thin film deposited at 15 mTorr was approximately less than 100 nm, while thin film deposited at 5 mTorr shows grains with size around to 200 nm. At lower pressure, larger grains generated due to coalescence of small grains and diffusion of atoms pressure are observed. Grain boundaries are visible at higher pressures in both sputtering systems.

The grains of the films deposited by RF-Sp are more homogeneous in size and shape than the grains composing DC-Sp films.



a)



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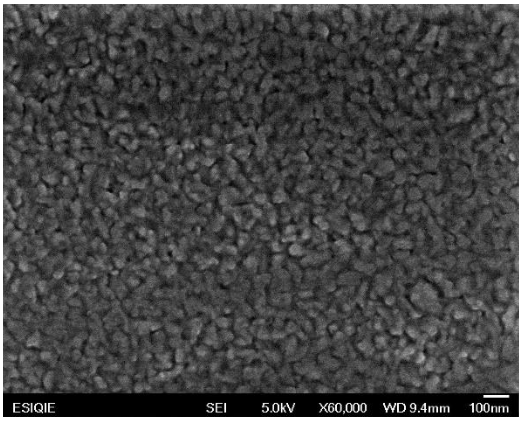

c)

Figure 5. Morphology images for Sb_2Te_3 by RF-Sp as a function of the deposition pressure: a) 5 mTorr, b) 10 mTorr and c) 15 mTorr.

Atomic composition and resistivity

In Figure 6, we can observe the values of Sb and Te atomic composition (At% Sb and Te) and the resistivity that were obtained for DC samples as a function of deposition pressure. The resistivity decreases, while the Sb atomic composition increases and Te atomic composition decreases these last two slightly when the deposition pressure decrease at the lowest value of 5 mTorr.

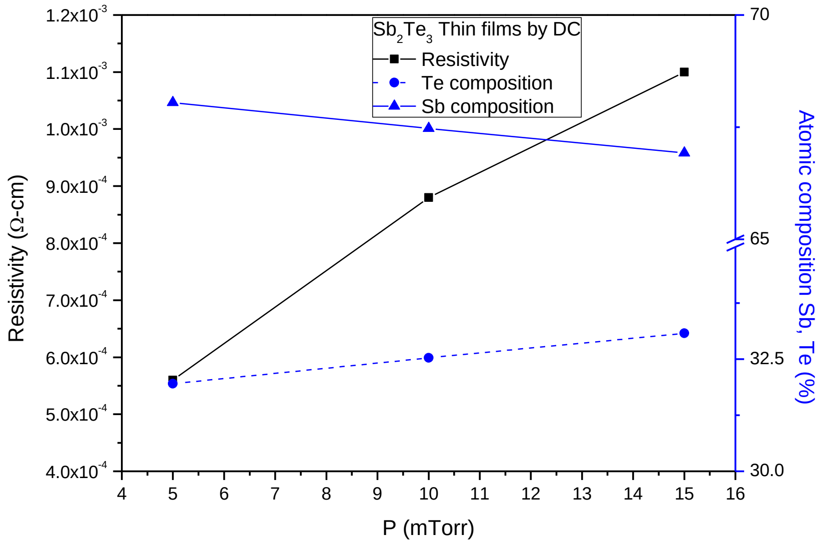

Figure 6. Resistivity and Sb, Te atomic composition for Sb_2Te_3 thin films deposited by DC-Sp as a function of deposition pressure.

Figure 7, shows the Sb and Te atomic composition and resistivity of the RF-Sp samples as a function of deposition pressure. We observed that the resistivity is reduced when deposition pressure decreases to 5 mTorr, while Te atomic composition increases and Sb atomic composition slightly diminishes as a function of deposition pressure.

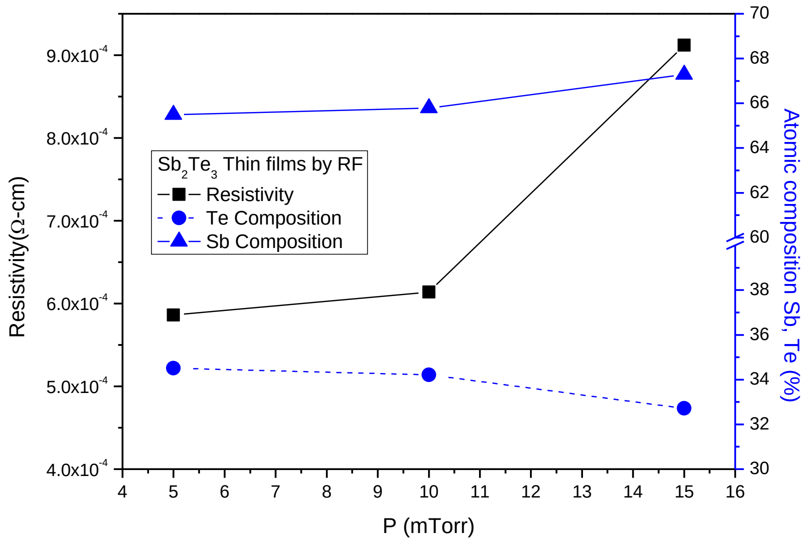

Figure 7. Resistivity and Sb, Te atomic composition for Sb_2Te_3 by RF-Sp as a function of deposition pressure.

While, other authors report that the conductivity is correlation to the grain size (12), we found that the resistivity is a correlation to the Sb and Te atomic composition too. On the other hand, when the deposition pressure decrease inside of the RF sputtering system, we obtained thin films with larger grains, a larger amount of Te in the composition and the resistivity decrease (conductivity increase) according to Bo Fang, et al (12). These variations have a positive influence on the electrical resistivity. Overall, these changes drastically affect the electrical transport properties of the Sb_2Te_3 thin films deposited by two sputtering systems, giving rise to the decreased resistivity.

In both experimental sputtering systems, we obtained an At% (Te/Sb) relation approximately close to 0.5 and resistivity value close to $6x10^{-4}$ Ω-cm (conductivity $1.6x10^{5}$ $(\Omega\text{-m})^{-1}$) according to Eliana et al. for Sb_2Te_3 thin films growth by co-evaporation technique on borosilicate glass at 230°C substrate temperature.

EDS analyses

In the Table II, shows the experimental EDS results with the Sb and Te atomic elements in the Sb_2Te_3 thin films for both sputtering systems.

Table II. Experimental EDS results for Sb2Te3 thin films deposited by DC and RF Sputtering system.

Sputtering-System	DC – Sp			RF – Sp		
Sample name	DC3	DC1	DC2	RF3	RF1	RF2
P (mTorr)	5	10	15	5	10	15
% Sb	68.05	67.47	66.92	65.79	65.49	67.28
% Te	31.95	32.53	33.08	34.51	34.21	32.72

The DC3 sample has the highest growth rate of 12.5 nm/min (thickness) and has the lowest Te atomic composition (31.95%) for the DC-Sp samples and the RF3 sample has the highest growth rate of 8.8 nm/min (thickness) and has the highest Te atomic composition (34.51%) for the RF-Sp samples; both samples were deposited at 5 mTorr of pressure. This result shows that Sb_2Te_3 thin films were Sb-rich and Te-rich due to increase evaporation during the growth process at lower deposition pressure. Moreover, if the deposition pressures decrease the atomic composition of Te decrease for DC-Sp films and increase for RF-Sp films.

In table II, we can observe that a slight increase in atomic composition at.% Sb occurs when the deposition pressure decreases for the DC-Sp samples and on the other hand a slight decrease in atomic composition at.% Sb occurs when the deposition pressure decrease for the RF-Sp samples

The EDS analysis reveals the presence of the elements of Sb_2Te_3 and glass (substrate) as seen in figure 8; however, the intensity of the peak associated with the oxygen (O) in relation to the intensity of the peak associated with the Silicon (Si), indicates a high amount of O, then maybe create oxides which could result to possible contamination of the sample. Nevertheless, no one diffraction line related to oxides of Sb or Te were observed in the XRD patterns of the Sb_2 Te_3 films.

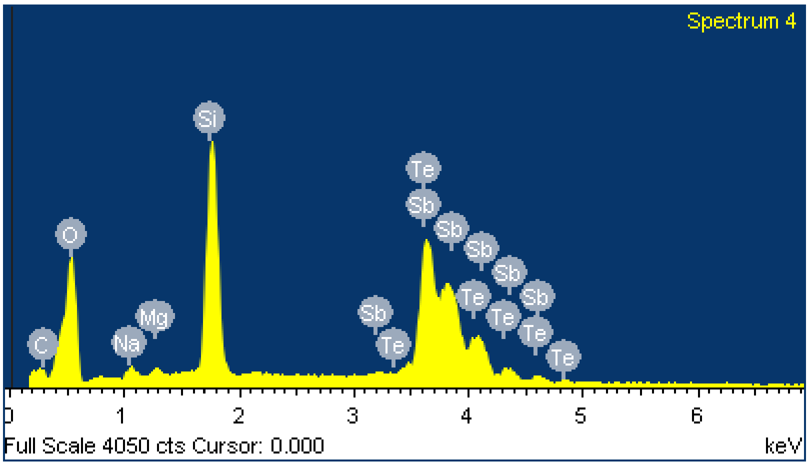

Figure 8. EDS spectrum of RF2 sample that shows the elements of Sb_2Te_3 and glass.

On the other hand, we found that some samples show certain porosity, for this reason a basic porosity study it was included. Figure 9, shows the influence of deposition pressure on the percent porosity of Sb_2Te_3 thin films grown by DC and RF-Sp and the images inserted, show the porosity of the films (figure 4 and 5). The porosity of Sb_2Te_3 thin films grown by DC-Sp is between 6-9.5%, when the sputtering pressure varies from 5 to 15 mTorr. When the deposit pressure increases from 5 to 15 mTorr, the porosity of Sb_2Te_3 thin films growth by RF-Sp decreases since 8.5 to 6%, approximately; according to Shen et al.

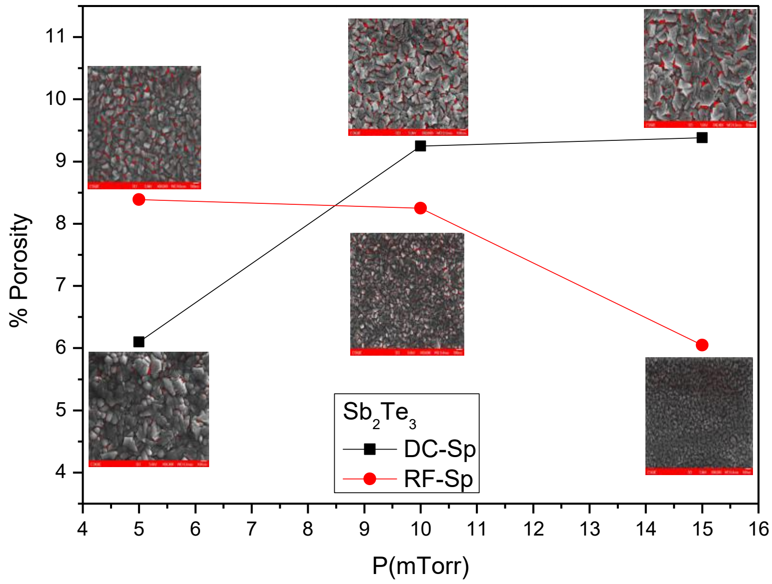

Figure 9. % Porosity of the Sb_2Te_3 thin film vs. deposition pressure for DC and RF-Sp.

In summary, the influence of deposition pressure on the properties of Sb_2Te_3 thin film by DC and RF sputtering system and its relationship with XRD pattern, morphological and porosity characteristic, electrical resistivity and %Te/Sb was studied.

5. Conclusions

We show the deposition pressure effects on the growth of Sb_2Te_3 thin films processed by DC and RF sputtering. For the Sb_2Te_3 samples deposited by DC-Sp and RF-Sp, the thickness increased systematically with the decreasing deposition pressure so that greater growth rate was obtained at lower pressures. The structural characteristics show that deposition pressure decrease promotes higher crystalline quality for DC-Sp and RF-Sp systems, but Sb_2Te_3 thin films by DC-Sp are of higher crystalline quality respect to RF-Sp. For the morphology, grains size is close to 100 nm for DC-Sp and RF-Sp and the grains are more compact at lower pressures. A greater compaction of grains implies a reduction in the pinholes, which promotes a lower resistivity value, close to $5.8x10^{-4}$ Ohm-cm, for each respective sputtering system, this property is very desirable for back surface field in thin films solar cells application. In addition to these low pressures (5 mTorr) the Sb atomic composition is highest of 68.05% for DC-Sp and the Te atomic composition is highest of 34.21% for RF-Sp. The SEM images and porosity characteristics of the thin films deposited at different pressures show that in general, the Sb_2Te_3 thin films grown by DC-Sp are more porous that the RF-Sp samples. In summary, the structure, morphology, layer composition and the resistivity of Sb_2Te_3 thin films depend on the type of sputtering system used and the deposition pressure. Adding to the pressure within the important variables to consider with it objective to obtain optimal morphological layers with great homogeneity, compaction and lower resistivity.

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