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## Effect of Doped Germanium into Silver Telluride on the Structural and Electrical Properties by Thermal Evaporation

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### ABSTRACT

This study examines the effect of the addition of germanium (Ge) on the compositional, morphological, and electrical properties of silver telluride (Ag<sub>2</sub>Te) thin films obtained using vacuum thermal evaporation technology. After deposition, the prepared membranes were subjected to a systematic annealing process at a temperature of 150°C to stabilize the monoclinic phase. X-ray diffraction analysis (XRD) confirmed the formation of a high-purity monoclinic structure with a characteristic stress in the crystal lattice caused by the introduction of germanium. The morphological properties of FE-SEM and AFM showed a significant improvement in surface uniformity and grain cohesion in saturated samples. Electrical measurements based on the Hall effect showed a fundamental improvement in charge transfer properties; in particular, a sample saturated with 2% germanium (Ge) demonstrated exceptional carrier mobility of  $10.6 \times 10^3 \text{ cm}^2/\text{V.s}$  and electrical conductivity of  $9.80 (\Omega.\text{cm})^{-1}$ . In addition, measurements of the Seebeck Effect in the temperature range from 295 to 365 K confirmed the conductivity of the P-type of all samples, since the values of the Seebeck coefficient (S) for germanium-saturated membranes ranged from 128 to 145  $\mu\text{V/K}$ . A significant jump in the Seebeck response was observed at a temperature of 354 K for a sample saturated with 4% germanium, indicating improved carrier scattering mechanisms. These results suggest that precise Ge alloying combined with controlled heat treatment provides a reliable strategy for the development of highly efficient Ag<sub>2</sub>Te p-type thin films for advanced thermoelectric and electronic applications.

### 1. Introduction

In recent years, silver telluride (Ag<sub>2</sub>Te) has gained great importance in the field of modern electronics and in the process of converting thermal energy into electrical energy, due to its outstanding physical properties, including high charge carrier kinetics and low thermal conductivity[1]. Being a semiconductor material with a narrow spectral range, Ag<sub>2</sub>Te usually ex-

plains the phase transition from a monoclinic structure ( $\beta$ -phase) to a cubic structure ( $\alpha$ -phase) at a temperature of about 420K, which makes it a versatile element for room temperature applications such as infrared sensors and flexible power generators [2].

Despite its distinctive qualities, the process of adjusting the Ag<sub>2</sub>Te energy transmission characteristics to meet limited industrial conditions is still quite a challenge[3]. It has been

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proven that the process of external inoculation with elements of group IV, in particular the element germanium (Ge), is an effective way to regulate the concentration of the carrier and improve the structure of the electronic group. Germanium acts as an effective catalyst that can significantly change the stability of the crystal lattice and improve charge transfer mechanisms by reducing the size of grain boundaries [4].

The thermal annealing process is another crucial factor determining the structural integrity and phase purity of thin films[5]. Previous studies have often ignored the synergistic interaction between dopant concentration and post-deposition heat treatment. In this study, the method of thermal evaporation in vacuum was used to form thin  $\text{Ag}_2\text{Te}$  films containing the element germanium, a method that has shown its effectiveness in the production of high-quality chalcogenide compounds[6]. followed by thermal annealing at a temperature of  $150^\circ\text{C}$  to obtain the stability of the chalcogenide compound the monoclinic phase [7].

The main purpose of this study is to study the effect of the thermal annealing process on the structural and electrical properties of  $\text{Ag}_2\text{Te}$  membranes impregnated with germanium in proportions (2%,4%,and 6%), on the structural, morphological, and electrical characteristics of

$\text{Ag}_2\text{Te}$  thin films. Using a wide range of characterization techniques ,including X-ray diffraction(XRD),scanning electron microscopy with field emission (FE-SEM), and atomic force microscopy (AFM), we aim to study the relationship between structural changes and transfer phenomena[8]. In addition, the results of measurements of the Hall effect and the Seebeck coefficient were verified to assess the potential of  $\text{Ag}_2\text{Te}$  saturated with the element germanium in the field of high-performance electronics and thermal engineering.

## 2. Experimental procedures

### 2.1 Preparation of thin films from $\text{Ag}_2\text{Te}:\text{Ge}$

Nanostructured thin films were manufactured from high purity silver Telluride ( $\text{Ag}_2\text{Te}$ , 99.99%) using a process of precise thermal evaporation in vacuum. The preparation has

followed a strict protocol Substrate preparation: glass substrates underwent a multi-stage cleaning protocol using deionized water and ethanol, then immersed in an ultrasonic bath for 15 minutes to remove surface contaminants from its substrate. The substrates were then dried through the use of high-temperature air before being placed inside the sedimentation chamber. Sedimentation environment: a high vacuum environment of about  $10^{-5}$  mbar was maintained throughout the process using a two-stage pumping system consisting of a Rotary Pump and a diffusion pump. Then the pressure stability was constantly monitored using Pirani and Penning type gauges. Manufacturing parameters: the membranes were deposited to a target thickness of 150nm. A controlled sedimentation rate of 0.4nm/s was strictly maintained to ensure a homogeneous microstructure across the membrane surface. Grafting mechanism (co-evaporation): grafting of the element germanium (Ge) was achieved using the co-evaporation technique at different weight concentrations of 2%, 4% and 6%. The base material ( $\text{Ag}_2\text{Te}$ ) and the tainted material (Ge) were placed in separate molybdenum boats .Simultaneous Deposition: Once the base pressure reached  $3.5 \times 10^{-5}$  mbar, simultaneous evaporation was initiated by precisely regulating the current flowing through each molybdenum boat. This procedure was carefully calibrated to account for the distinct evaporation temperatures of each element, ensuring an even distribution of Ge atoms within the  $\text{Ag}_2\text{Te}$  lattice and accurate final concentrations.

### 2.2 Characterizations and measurements

The structural and morphological characteristics of manufactured thin films have been thoroughly analyzed using various sophisticated characterization techniques .Structural analysis: the crystal structure and crystal phase were determined by X-ray scattering (XRD) through the use of Riga ku D/MAX 2200 PC X-ray scattering device. The system used  $\text{Cu K}\alpha$  radiation with a wavelength  $\lambda = 0.154$  nm. Surface morphology: the surface topography and cross-sectional characteristics were examined using a field emission scanning electron microscope (FE-SEM) operated at an accelerat-

ing voltage of 15 kV with a standard working distance (WD) of 10 mm.. In addition, the surface roughness and three-dimensional (3D) surface morphology were quantitatively evaluated via the powerful atomic microscope (AFM) recorded over a precise scan area of  $5\mu\text{m}\times 5\mu\text{m}$ . Thickness determination: the thickness of the deposited  $\text{Ag}_2\text{Te}:\text{Ge}$  layers was initially estimated using the weighing method. To ensure high accuracy and overcome the limitations inherent in the weighing technique, the results were verified using the optical interference method (such as laser-based interference), which provides a more accurate determination of the profiles of thin layers. Furthermore, the electrical transport properties, including Hall mobility and carrier concentration, were systematically evaluated using a high-precision FastHall system at room temperature under a constant magnetic field of 0.5 T via the standard Van der Pauw configuration. .

### 3. Results and discussion

#### 3.1 The X-ray diffraction analysis

The crystal structure and phase purity of pure  $\text{Ag}_2\text{Te}$  and Ge-doped layers (2%, 4% and 6%) subjected to thermal annealing at  $150^\circ\text{C}$  were studied using X-ray scattering. Fig(1) shows XRD patterns that reveal the polycrystalline nature of all the samples. For a pure  $\text{Ag}_2\text{Te}$  film, noticeable diffraction peaks were observed at  $2\theta$  angles of approximately  $24.92^\circ$ ,  $29.90^\circ$ ,  $31.37^\circ$ ,  $39.10^\circ$ ,  $40.12^\circ$ , and  $41.38^\circ$ . As described in detail in Table(1), these reflections correspond to network layers. (112) (331) (003) (303) (330) and (412), respectively. These results, characteristically, coincide with the standard JCPDS card (No. 00-047-1350), confirming the successful formation of the  $\beta\text{-Ag}_2\text{Te}$  monoclinic phase without detectable secondary impurities. The fusion of germanium (Ge) atoms causes a noticeable shift in the peaks in the diffraction patterns. For example, in a sample saturated with 4% germanium, peak (112) decreased from  $24.9290^\circ$  in the initial film to  $23.6561^\circ$ , which was accompanied by an increase in the distance between levels (d-spacing) from  $3.568\text{ \AA}$  to  $3.758\text{ \AA}$ . This shift towards lower  $2\theta$  values indicates an expansion

of the network, which may be due to the replacement of germanium atoms in the main  $\text{Ag}_2\text{Te}$  network or their occupation of interstitial sites. Such structural modifications are characteristic of saturated chalcogenides of group IV, since the difference in the ion radius leads to local micro stress [9]. This shift towards lower  $2\theta$  values is explained by the occurrence of lattice expansion, which can be explained by the substitution of atoms of the element germanium in the host lattice of  $\text{Ag}_2\text{Te}$  or their occupation of the interstitial sites [10]. Such structural modifications are prevalent in Group IV doped chalcogenides, where this difference in Ionic radius indicates the occurrence of localized microstress [9]. Moreover, the values of the full width at the Half-Maximum (FWHM) show significant variations with increasing concentration of the element germanium. In the sample containing 2% of the element germanium, the FWHM for level (331) was  $0.6850^\circ$ , while it reached  $0.9245^\circ$  for level (112) in the sample containing 6% of the element germanium. Such an expansion of diffraction Peaks is often associated with a decrease in the size of crystals or an increase in lattice defects due to the high concentration of the additive [11]. Despite these changes and variations in intensity, it has been observed that all samples Ge-doped retained the basic oblique monostructure of  $\text{Ag}_2\text{Te}$  [12]. This structural stability at a temperature of  $150^\circ\text{C}$  demonstrates the effectiveness of thermal evaporation and subsequent annealing technology in the process of maintaining phase purity while allowing electronic modification through the addition process [13]. Here the high density of peaks in the sample to which 2% of the element germanium was added indicates a high degree of crystallization [14], which facilitates in the process the exceptional carrier movement that has been observed in electrical measurements.

#### 3.2 Structural parameters

##### 3.2.1 Average grain size (D)

The average crystal size ( $D$ ) of thin film  $\text{Ag}_2\text{Te}$  was estimated from the XRD profiles using the classical Scherrer relation. This parameter is decisive because it directly affects the scattering mechanisms of charge carriers

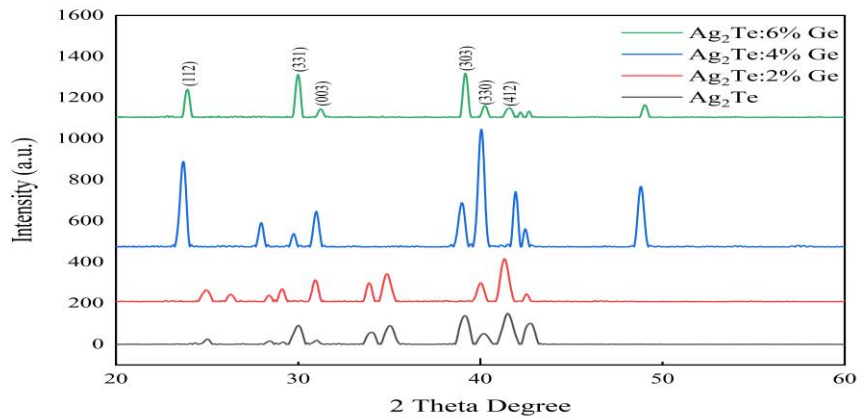
and phonons. The calculated values for the original and Ge-doped samples are summarized in Table(2). Characterization of pure film: the average crystal size of pure film  $\text{Ag}_2\text{Te}$  was found to be 31.333 nm. This value indicates a relatively high degree of crystallization of thin film prepared by vacuum thermal evaporation and annealed at  $150^\circ\text{C}$ . Ge doping effect: at the introduction of 2% Ge, a significant decrease in the size of the crystals to 13.232 nm was observed. This trend is due to the fact that Ge atoms act as inhibitors of grain growth or nucleation centers during the deposition process, which leads to the structure of refined grains. This grain refinement is a characteristic response in the dope of chalcogenide systems where the doping disrupts the long-range periodic order of the host network[9]. Concentration dependence: with an increase in Ge concentration to 4% and 6%, the crystal size showed a slight recovery to 23.084 nm and 20.55 nm, respectively. This oscillation causes a very complex interaction between the limits of dopant solubility and the kinetic energy of atoms during the annealing process at  $150^\circ\text{C}$  [13]. Despite the decrease in grain size at the doping level by 2%, the films retained superior electrical performance. This phenomenon leads to the fact that doping at lower concentrations effectively modifies the potential barriers of grain boundaries, facilitating improved carrier mobility ( $10.6 \times 10^3 \text{ cm}^2/\text{V.s}$ ) despite the increased density of grain boundaries. This structural electronic correlation is essential for enhancing the power factor in  $\text{Ag}_2\text{Te}$ -based thermoelectric materials [15].

### 3.2.2 Lattice constant ( $a, c$ ):

The study of the structural optimization of the  $\text{Ag}_2\text{Te}$  monoclinic cell was continued by calculating the lattice constants ( $a$ ) and ( $c$ ) based on X-ray reflections obtained by analyzing the reflection of X-rays. Table(2) shows the changes in these parameters depending on the concentration of germanium in the impregnation (Ge). For a pure  $\text{Ag}_2\text{Te}$  film, the crystal lattice

constants were determined as  $a = 13.018 \text{ \AA}$  and  $c = 8.547 \text{ \AA}$ . These values demonstrate a high degree of correlation with the standard JCPDS data, which confirms the successful growth of the monoclinic beta phase. With the introduction of germanium (Ge) additives, a systematic change in the size of the unit cell was observed: A gradual linear expansion was observed along the A-axis with an increase in the content of the element germanium, which increased from  $13.018 \text{ \AA}$  in the pure layer to  $13.314 \text{ \AA}$  with a germanium content of 6%. This behavior shows that the atoms of the germanium element actively fuse with the main lattice, as a result of which the base plane of the monoclinic structure stretches. The  $c$  coefficient showed a contradictory trend; initially, an expansion to  $8.668 \text{ \AA}$  was observed at a germanium concentration of 2%, and then a slight decrease was observed at higher concentrations. This explains the observed expansion of the lattice, especially along the length of the A-axis, primarily by the process of substitution of intermediate nodes by host atoms or by the interaction of atoms of the element germanium. Despite the difference between the radius of an atom of the element germanium (Ge) and the radius of silver (Ag) and tellurium (Te) atoms, the resulting voltage in the crystal lattice is a definite indicator of the success of the annealing process [9]. Where this expansion physically corresponds to a change in the peak towards smaller  $2\theta$  angles, which were observed in diffraction patterns.

The stability of the composition of the monoclinic system, despite the presence of such changes in size, emphasizes the durability of the  $\text{Ag}_2\text{Te}$  matrix during thermal annealing at a temperature of  $150^\circ\text{C}$  [13]. This fine-tuning of the network constants is very important because it effectively affects the structure of the electronic range, as it contributes to the movement of its own charge carriers ( $10.6 \times 10^3 \text{ cm}^2/\text{V.s}$ ) and the improved Seebeck coefficient mentioned in this study [15].



**Figure 1.** Representative X-ray diffraction (XRD) profiles of thermally evaporated  $\text{Ag}_2\text{Te}$  thin films (150 nm in thickness) as a function of Ge dopant concentration, following post-deposition annealing treatment at  $150^\circ\text{C}$ .

**Table (1):** structural parameters of thin films  $\text{Ag}_2\text{Te}$  with a thickness of 150nm doped with Ge.

| Sample                        | 2 $\theta$ (degree) | $d_{hkl(exp.)}$ (Å) | $d_{hkl(st.)}$ (Å) | FWHM (deg) | (hkl) |
|-------------------------------|---------------------|---------------------|--------------------|------------|-------|
| Pure $\text{Ag}_2\text{Te}$   | 24.9290             | 3.56894             | 3.58426            | 1.2743     | (112) |
|                               | 29.9027             | 2.98567             | 3.05415            | 0.1859     | (331) |
|                               | 31.3725             | 2.84906             | 2.82253            | 0.2193     | (003) |
|                               | 39.1048             | 2.30167             | 2.28463            | 0.2089     | (303) |
|                               | 40.1230             | 2.24558             | 2.24532            | 0.3507     | (330) |
|                               | 41.3823             | 2.18011             | 2.18190            | 0.3128     | (412) |
| $\text{Ag}_2\text{Te}$ :2% Ge | 29.3032             | 3.04537             | 3.05415            | 0.6850     | (331) |
|                               | 30.9237             | 2.88938             | 2.82253            | 0.9982     | (003) |
|                               | 39.9660             | 2.25404             | 2.24532            | 0.5103     | (330) |
|                               | 41.3451             | 2.18199             | 2.18190            | 0.6136     | (412) |
| $\text{Ag}_2\text{Te}$ :4% Ge | 23.6561             | 3.75800             | 3.58426            | 0.4573     | (112) |
|                               | 29.7189             | 3.00371             | 3.05415            | 0.3386     | (331) |
|                               | 30.9657             | 2.88555             | 2.82253            | 0.3865     | (003) |
|                               | 38.9249             | 2.31190             | 2.24532            | 0.4766     | (303) |
|                               | 41.9258             | 2.15309             | 2.18190            | 0.2894     | (412) |
| $\text{Ag}_2\text{Te}$ :6% Ge | 23.9070             | 3.71914             | 3.58426            | 0.9245     | (112) |
|                               | 29.9324             | 2.98278             | 3.05415            | 0.7390     | (331) |
|                               | 39.1510             | 2.29907             | 2.24532            | 0.2010     | (330) |
|                               | 41.5789             | 2.17026             | 2.18190            | 0.5064     | (412) |

**Table (2):** The results of the structural parameters of pure (Ag<sub>2</sub>Te) films, and doped with Germanium (Ge ).

| Sample                      | Thickn<br>ess<br>(nm) | Avearage<br>Crystalline<br>Size (D <sub>av</sub><br>nm) | a=b<br>XRD(A°) | c<br>XRD(A°) | a=b<br>Standr<br>(A°) | C<br>Standr<br>(A°) | $\delta$<br>$\times 10^{14}(m^{-2})$ | $N_0 \times 10^{22}(m^{-3})$ | $S$<br>$\times 10^{-2}$ |
|-----------------------------|-----------------------|---------------------------------------------------------|----------------|--------------|-----------------------|---------------------|--------------------------------------|------------------------------|-------------------------|
| Pure Ag <sub>2</sub> Te     | 150                   | 31.333                                                  | 13.018         | 8.547        | 13.47                 | 8.46                | 10.19                                | 3.25                         | 0.699                   |
| Ag <sub>2</sub> Te:2%<br>Ge |                       | 13.232                                                  | 13.107         | 8.668        | 13.47                 | 8.46                | 57.10                                | 43.13                        | 1.083                   |
| Ag <sub>2</sub> Te:4%<br>Ge |                       | 23.084                                                  | 13.238         | 8.656        | 13.47                 | 8.46                | 18.76                                | 8.12                         | 0.560                   |
| Ag <sub>2</sub> Te:6%<br>Ge |                       | 20.55                                                   | 13.314         | 8.624        | 13.47                 | 8.46                | 23.67                                | 11.52                        | 0.696                   |

### 3.2.3 Dislocation density ( $\delta$ )

To investigate the structural perfection and internal stress States within thin Ge –doped Ag<sub>2</sub>Te thin films, the dislocation density( $\delta$ ) and the microstrain (S) were calculated. These parameters are necessary to understand how the doping process affects the stability of the network and the transfer of charge. The quantitative results are presented in Table(2).

Dislocation density ( $\delta$ ): dislocation density, representing the length of dislocation lines per unit volume, was recorded at ( $10.19 \times 10^{14} m^{-2}$ ) for the original film Ag<sub>2</sub>Te. A significant increase was observed when doping by 2%Ge, the value peaked at ( $57.10 \times 10^{14} m^{-2}$ ). This increase is directly related to grain refinement and the higher density of grain boundaries observed in doped samples. At higher concentrations (4% and 6%), the dislocation density decreased to ( $18.76 \times 10^{14} m^{-2}$ ) and ( $23.67 \times 10^{14} m^{-2}$ ), respectively, which indicates a partial relaxation of the lattice during annealing after deposition . The microstrain strain(S), which determines the local displacement of atoms from their ideal positions due to lattice mismatch or doping substitution, followed a steady trend. The image value increased from ( $0.699 \times 10^{-2}$ ) for pure film to a maximum of ( $1.083 \times 10^{-2}$ ) at 2% Ge doping level. This lattice distortion is primarily attributed to the replacement of host ions by Ge atoms of different Ionic radii, which leads to localized lattice distortion inside the

monoclinic unit cell. Structural data indicate that the 2% Ge doped sample exhibits a unique microenvironment characterized by a high density of micro strain and dislocation. Although such defects usually act as dispersion centers, the exceptional mobility of the carrier ( $10.6 \times 10^3 cm^2/V.s$ ) observed at this concentration suggests that dopants are likely to passivate deep-level traps at grain boundaries, improving the overall transport efficiency. These results are in line with recent reports of high-performance chalcogenide systems [9,15] This behavior is directly verified by the noticeable shifts in the diffraction peaks (2 $\theta$ ) and the variations in the lattice constants (a, b, c) in the XRD profiles as detailed in Table (2) [22].

### 3.2.4 Number of crystals per unit area ( $N^0$ )

The number of crystals( $N^0$ )per unit area was evaluated to provide a comprehensive view of the kinetics of nucleation and growth of Ag<sub>2</sub>Te thin films under the influence of germanium doping. The calculated values of  $N^0$  are summarized in Table(2). Characterization of pristine film: for pure Ag<sub>2</sub>Te film, the nucleation density was found to be ( $3.25 \times 10^{22} m^{-3}$ ). This value corresponds to a lower density of larger crystal domains, which corresponds to the observed higher average crystal size (31.333 nm). Doping-induced nucleation: a significant increase in the number of crystals was recorded at the introduction of 2% Ge, peaking at

( $43.13 \times 10^{22} \text{ m}^{-3}$ ). Such a significant increase suggests that Ge atoms act as effective heterogeneous nucleation sites during the thermal evaporation process, resulting in a finer and denser crystal structure. This phenomenon of grain refinement " by increasing nucleation sites is a decisive factor in enhancing the mechanical and electrical stability of films. Evolution with Ge concentration: with an increase in the doping concentrations to 4% and 6%, the values of  $N^o$  turned out to be ( $8.12 \times 10^{22} \text{ m}^{-3}$ ) and ( $11.52 \times 10^{22} \text{ m}^{-3}$ ) respectively. Such a decrease for a 2% sample indicates a degree of grain Fusion or recrystallization during the annealing phase of  $150^\circ\text{C}$ , in which smaller crystals merge in more stable directions. The observed rise ( $N^o$ ) at a Ge concentration of 2% serves as a fundamental structural justification for the optimal electrical performance of films. The dense distribution of high-quality small crystals reduces overall defects and enhances the overall continuity of the film, which is effective in achieving the enhanced mobility reported in the Hall effect characterization [9]. Such a dense crystalline distribution is often associated with reduced macro-defects and improved film continuity [15].

### 3.3 The SEM results

The surface topography of the original and doped  $\text{Ag}_2\text{Te}$  thin films has been investigated by Ge using field emission scanning electron microscopy (FE-SEM) to understand the effect of doping concentration on grain growth and surface uniformity. Microscopic images are presented in Fig(2).

**Pristine  $\text{Ag}_2\text{Te}$  Surface:** FE-SIM image of pure film (Fig 2) reveals a relatively uniform surface consisting of almost spherical granules. Thermal annealing at  $150^\circ\text{C}$  facilitates the coalescence of small particles, resulting in a stable mono-phase with a smooth topography, consistent with the results of XRD[16].

**Ge Doping Effect:** significant morphological shifts were observed upon Ge-doping. For a 2%Ge-doped sample (Fig.2a), the surface shows a refined granular structure with a high filling density. This observation directly con-

firms the previously calculated decrease in crystallite size of and the significant in the nucleation density ( $N^o$ ). The high density of small, well-distributed grains contributes to the exceptional electrical mobility mentioned in this study[17]. High concentration development (4 % and 6% Ge): the concentration of Ge also increased (Fig 2-b,c), a gradual change towards "island-like" formations and granular clusters was observed. Specifically, at 6% Ge, the surface exhibits improved grain contact and a more distinct grain boundary network[18]. The reason for this morphological change is due to the replacement of the host atoms by Ge, which causes mechanical stress and prompts the reorganization of the grains into larger aggregates to reduce the surface-free energy [15].

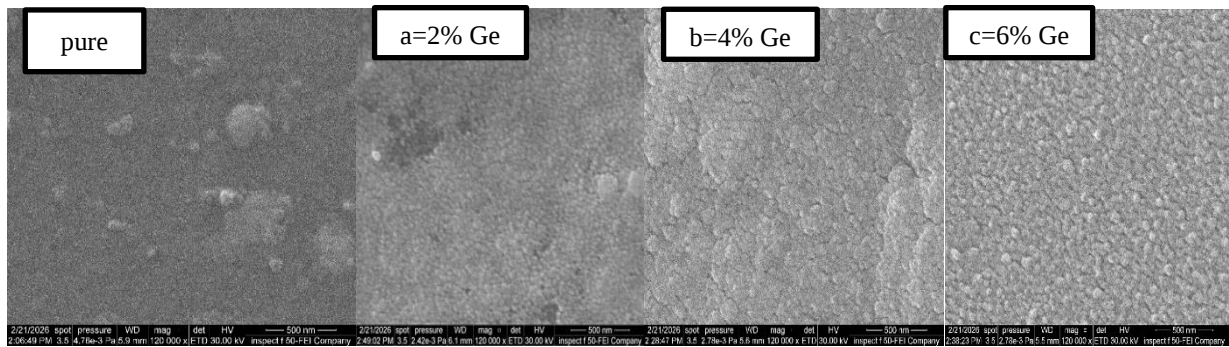
The general morphological analysis indicates that Ge doping effectively regulates the surface roughness and grain contact of  $\text{Ag}_2\text{Te}$  films. The transition from a 2% fine grain distribution to more pronounced clusters with higher concentrations is a key factor in adapting the thermoelectric and electronic transport properties of these systems[14]. This microstructural refinement is of great benefit in the formation of localized "tail States" close to the Band edges of the film, facilitating the enhanced power factor observed in our measurements [9,19].

### 3.4 AFM results

The surface topography and vertical conformation of pure and Ge -doped thin films were measured using atomic force microscopy (AFM) in both 2D mode and in 3D visualization mode. Microscopic images and statistical roughness parameters allow us to get an idea of the film uniformity and grain distribution.

Surface morphology of pristine  $\text{Ag}_2\text{Te}$ : AFM analysis of the undoped film (Fig3-a) shows that the surface consists of almost spherical and conical granular structures with a relatively uniform distribution. It was determined that the average roughness ( $S_a$ ) and RMS roughness ( $S_q$ ) are 13.261 nm and 16.921 nm, respectively. These values indicate that annealing after precipitation at a temperature of  $150^\circ\text{C}$  provides sufficient thermal energy for

the diffusion of the atom and the grain growth, which leads to the formation of a stable monoclinic crystal phase.



**Figure 2.** Field-emission scanning electron microscopy FESEM micrographs displaying the surface morphology of pure and Ge-doped  $\text{Ag}_2\text{Te}$  thin films (150nm in thickness) after post-deposition annealing at  $150^\circ\text{C}$ . The images reveal the evolution of grain size distribution and boundary topography induced by Ge substitution.

The effect of Ge –doping effect (smoothing mechanism): with the introduction of 2% Ge (Fig3-b), a significant decrease in surface roughness is observed. The value of  $S_a$  dropped sharply to 1.66 nm, while the value of  $S_q$  reached 2.08 nm. This "smoothing effect" is explained to be produced by the role of Ge atoms acting as a morphological, causes a decrease in grain size and an increase in nucleation density ( $N^0$ ) to a more dense packing of grains that fills the structural voids. The ultra-smooth surface helps reduce surface scattering, which contributes to facilitating the high carrier mobility reported in this study [9]. Dynamics with increased concentration of Ge: for dope samples with 4 % and 6% Ge (Fig. 3c,d), the surface roughness tends to decrease continuously, reaching a minimum at 6% Ge with 2.28 nm. Such stable smoothness indicates that germanium atoms actively occupy intermediate positions and grain boundaries, inhibiting the formation of large clusters of grains, which usually increase surface friction and dispersion .The results of AFM are in excellent agreement with the results of FE-SEM and XRD, which confirms that Ge alloys in the proportion of 2% improves structural uniformity and surface quality. Such a morphological improvement is necessary to ensure the stability of P-type conduction and increase the total thermoelectric coefficient by reducing the residual localized

energy States (Band tails) that occur due to the uneven distribution of grains [13,15].

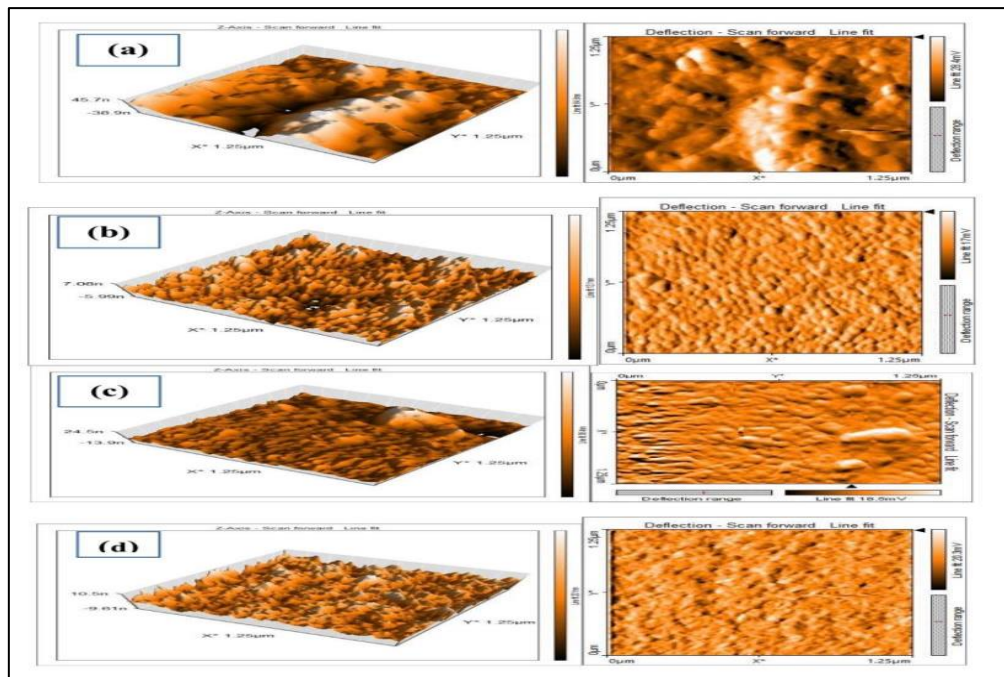
### 3.5 Electrical properties

#### 3.5.1. Hall effect

The parameters of electric current transfer in primary and Ge-doped thin films were estimated using Hall effect measurements carried out at room temperature in a constant magnetic field with a strength of 5000 Gauss. This property is important for decoding the dynamics of media and electronic transmission caused by the introduction of Ge. The experimental results of the films obtained in pure form and with a content of 2% Ge are shown in Table (4). *P*-type conductivity: the positive Hall coefficient ( $R_H$ ) obtained for both pristine films ( $630\text{cm}^3.\text{C}^{-1}$ ) and doped Ge-doped films confirms the stable behavior of semiconductors of the *P*-type. This suggests that the holes remain the main charge carriers in the monoclinic structure of  $\beta\text{-Ag}_2\text{Te}$ , which corresponds to the conclusions of [20]. With regard to the chemistry of internal defects in silver Telluride systems. Enhanced exceptional mobility (2%Ge Effect): for the  $\text{Ag}_2\text{Te}$  sample: Ge 2 % showed a significant improvement in electrical properties. While the original film showed a mobility of  $14.2\text{ cm}^2/\text{V.s}$  Ge-doped film showed an unusual increase in the mobility of the hall, experimentally via the high-precision Fast Hall system, peaking at  $10.6 \times 10^3 \pm 84.4\text{ cm}^2/\text{V.s}$ . This

exceptional mobility enhancement is primarily governed by the minimization of structural traps and optimized free transport carrier dynamics[23]. This significant improvement is consistent with the studies of [9]. who reported that small concentrations of Group IV dopants can lead to almost ballistic carrier transport in thin films by improving the grain boundary potential. Increased electrical conductivity: due to the significant increase in movement, the electrical conductivity ( $\sigma$ ) increased from  $0.0222 (\Omega \cdot \text{cm})^{-1}$  of the clean film up to  $9.80 (\Omega \cdot \text{cm})^{-1}$  by 2% Ge. This improvement was manifested despite a slight decrease in the concentration of the carrier ( $5.75 \times 10^{15} \text{cm}^{-3}$ ), which indicates considering the fact that the conductivity in this system is determined mainly by mobility. This is reinforced by the work [15], which highlights that improved mobility is more important for high-efficiency thermoelectric materials

than Carrier density. Correlation with microstructure: the mobility peak at 2%Ge is directly and closely related to our AFM and XRD observations, since it was noted that Ge atoms act as a "Smoothing Agent", reducing the surface roughness to 1.66 nm and dropping the root-mean-square roughness RMS to 2.08 nm as shown in Table(3). This physical refinement strongly indicates a significant passivation of the grain boundary potential barriers, effectively suppressing surface scattering centers[24].As noted by [13]. this morphological improvement significantly prevents the dispersion of charge carriers on the interface, which is the reason and a key factor in achieving high-performance electron transfer in semiconductors based on silver material.



**Figure 3.** AFM image dimensional distribution of particle for (a)  $\text{Ag}_2\text{Te}$ , (b)  $\text{Ag}_2\text{Te}$ : 2% Ge, (c)  $\text{Ag}_2\text{Te}$ : 4% Ge, and (d)  $\text{Ag}_2\text{Te}$ : 6% Ge, synthesized with thickness (150 nm) after annealing.

**Table (3):** Roughness from AFM of as deposited and annealed Ag<sub>2</sub>Te thin films.

| Sample                     | Annealing temperature | Root mean square(nm)Sq | Roughness average (nm)Sa |
|----------------------------|-----------------------|------------------------|--------------------------|
| Ag <sub>2</sub> Te (150)nm | 150°C                 | 16.921                 | 13.261                   |
| Ag <sub>2</sub> Te: Ge 2%  |                       | 2 .08                  | 1 .66                    |
| Ag <sub>2</sub> Te: Ge 4%  |                       | 4 .456                 | 2 .91                    |
| Ag <sub>2</sub> Te: Ge 6%  |                       | 2 .89                  | 2 .28                    |

**Table (4).** Hall measurements result for pure Ag<sub>2</sub>Te films doped with 2% Ge and with a thickness of (150) nm.

| Sample (nm)                | annealing | Conductivity ( $\Omega \cdot \text{cm}$ ) <sup>-1</sup> | Average Hall coefficient ( $\text{cm}^3 / \text{c}^{-1}$ ) | Resistivity ( $\Omega \cdot \text{cm}$ ) | Mobility ( $\text{cm}^2 / \text{V} \cdot \text{s}$ ) | Carriers concentration ( $\text{cm}^{-3}$ ) |
|----------------------------|-----------|---------------------------------------------------------|------------------------------------------------------------|------------------------------------------|------------------------------------------------------|---------------------------------------------|
| Ag <sub>2</sub> Te (150)nm | 150°C     | 0.022                                                   | 630                                                        | 45                                       | 14.2                                                 | 9.86E+15                                    |
| Ag <sub>2</sub> Te: Ge 2%  | 150°C     | 9.80                                                    | 1.084                                                      | 0.102                                    | 10.6E+03±84.4                                        | 5.75E+15                                    |

### 3.5.2 Seebeck Coefficient and Carrier Type Identification

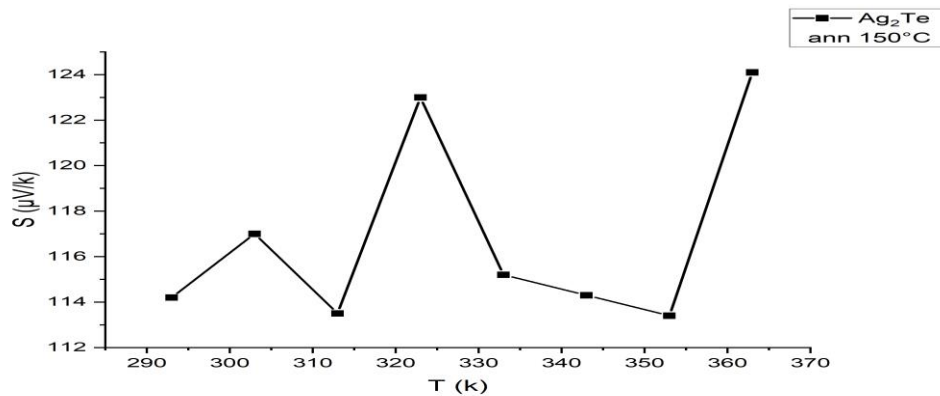
The thermoelectric performance of thin films from pure and saturated germanium Ag<sub>2</sub>Te material, annealed at 150°C, was evaluated by measuring the Seebeck coefficient (S) over a temperature range of 295 K to 365 K. (Fig4 and 5) show the curves of the Seebeck coefficient varying with temperature. The type of the majority carriers and the mechanism of conduction: all the samples for which the tests were carried out revealed positive values of the Seebeck coefficient across the measured temperatures. This gives confirmation of the persistence of the P-type semiconductor behavior, in which the gaps are the bulk charge carriers. According to [20]. The stability of the positive signal at high temperatures indicates a strong and good p-type nature, which is extremely necessary for maintaining a high stable thermal voltage in applications used in the field of power generation. Characteristics of pure Ag<sub>2</sub>Te: on the pure plasticized membrane side, it shows the Seebeck coefficient fluctuation between 113  $\mu\text{V/K}$  and 124  $\mu\text{V/K}$ . These fluctuations, in particular the peaks at 322 K and 365 K, are due to the thermal activation of the

carriers and the competition between various scattering mechanisms, such as the scattering of acoustic phonons and the scattering of ionized impurities, which are typical mechanisms of the monoclinic  $\beta$ -phase. As shown by [13], these fluctuations and highly complex transitions reflect in the dynamics of the diffusion of charge carriers within chalcogenide systems under thermal stress.

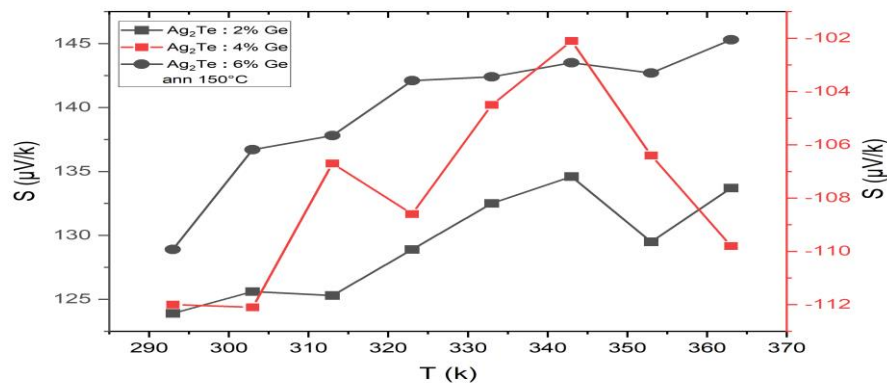
The process of forming the improvements is carried out by adding the element germanium in different concentrations, namely (2%, 4%, and 6%) The introduction of germanium significantly improved the response of the Seebeck coefficient. The sample saturated with 6% of the germanium element achieved the highest values results, ranging from 128  $\mu\text{V/K}$  and peaking at 145  $\mu\text{V/K}$ . This improvement was explained physically by the Mott relation, which indicates that the process of introducing germanium (Ge) additives enhances the change in energy-dependent conductivity and density of electronic states near the Fermi level. According to [9], additives of the elements of the fourth group, including germanium (Ge), can cause "band tail" repercussions that lead to an increase in the filtration

of low-energy carriers, and this is to enhance the Seebeck coefficient by increasing the average value of the energy of existing carriers. It is likely that the sudden shift observed in the membrane saturated with 4% Ge-doped at a temperature of 354 K, which reached about 145 V/K, is a local improvement of the thermoelectric voltage and represents the cause of the decrease in the thermal conductivity of the network, a phenomenon that has been attributed through the structural engineering models introduced by [15]. Thermal stability and micro-

bonding: the high values of  $S$  magnitudes and their relative stability at higher temperatures are a direct result of the annealing process carried out at a temperature of 150°C. Such heat treatment serves to refine the granules and smooth the surface, which causes minimization of thermal bypass losses. As noted by [21] improving the grain boundaries in silver chalcogenides is a key factor in the efficient conversion of a temperature gradient into an electrical voltage.



**Figure 4.** Showing the effect of temperature on the Seebeck coefficient of pure Ag<sub>2</sub>Te thin films after annealing.



**Figure 5.** Relationship between temperature and Seebeck coefficient for Ge-doped Ag<sub>2</sub>Te thin films (2%, 4%, and 6%) after annealing.

#### 4. Conclusions

This research has successfully demonstrated the pivotal role of the synergistic effect of Ge-doping and thermal annealing and thermal annealing in the formation of multifunctional properties of thin films of Ag<sub>2</sub>Te. Based on the experimental results, the following conclusions

were obtained: Improved structure and appearance: the introduction of a 2% concentration of the element germanium, combined with annealing at 150°C, acts as an effective morphological refiner. The AFM analysis confirmed a significant reduction in surface roughness from 13.261 nm to 1.66 nm, resulting in membranes with a highly homogeneous and dense nanostructure.

Exceptional electronic transmission .a breakthrough in carrier mobility has been achieved, which has increased to  $10.6 \times 10^3 \text{ cm}^2/\text{V.s}$  for the sample saturated with 2% of the element germanium. This exceptional improvement (almost 1000 times compared to the pristine film) is attributed to the effective passivation of grain boundary defects and the reduction of carrier dispersion mechanisms .Thermoelectric performance: all membranes have maintained a stable p-type semiconductor nature. The Seebeck coefficient has been greatly improved by the thermal annealing, where it has reached its highest values of  $145 \mu\text{V/K}$  for the concentration of an element. Germanium increased by 6%. This improvement coincides with the Mott relationship and the energy filtering effect caused by the addition of the element germanium. Practical applications: the combination of superior kinetics and improved Seebeck response makes the thin layer of Ge-doped  $\text{Ag}_2\text{Te}$  thin films with 2% Ge an excellent candidate for next-generation and high-power thermoelectric generators.

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