

Crystallization Ga-Sb-Te thin films in terms of Sheet resistance

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Received: 10 Feb. 2019, Revised: 12 July 2019, Accepted: 10 Aug. 2019

Published online: 1 Jan. 2020

Abstract: The present work investigates the sheet resistance, R_s , measurements versus temperature, T , for 1000 nm Ga-Sb-Te thin films at different heating rates ($\beta = 5, 10, 20, 30$ and 40 K/min) in the temperature range from 300 to 673 K. Then, the study of the thermal and electrical properties and thus we will reduce the time and save the effort. As well, the thermal and electrical analysis appears in a new format without the need for procedure the thermal measurements from bulk material of the investigated thin films. After that, the thermal and electrical properties carried out based on the sheet resistance, R_s , measurements as a function of the temperature. The activation energies of crystallization and the rest of thermal parameters such as the growth order parameter n , and the dimension order parameter m , have been computed. The activation energy, E_c , and Avrami index, n , were determined by analyzing the data using JMA methods. The results indicated that the transformation from amorphous to crystalline phases is a complex process includes different mechanisms of nucleation and growth. The change of activation energy with the volume of crystalline fraction was deduced. The crystalline phases for the studied film with heating rate, ($\beta = 5$ K/min), as example, were identified via x-ray diffraction (XRD).

Keywords: Sheet resistance, Ga-Sb-Te thin films; heating rates; crystallization kinetics; Avrami index.

1 Introduction

The chalcogenide materials are the key elements of continued technological advances made in the fields of optoelectronic, photonic, and magnetic devices. They have already been used in semiconductor devices, wireless communications, telecommunications, integrated circuits, transistors, rectifier, solar cells, light-emitting diodes, magneto-optic memories, photoconductors, audio and video systems, smart windows, computer chips [1, 2] *etc.* All these applications of these materials are due to their smaller phonon energies as compared to oxide glasses [3] and their better infrared transmission [4, 5]. Several publications have reported results associated with laser induced crystallization, speed of crystallization, properties of the amorphous material, dependence of carrier to noise ratio on the composition, *etc.* It has been found that both the temperature and speed of crystallization depend on the Sb/Te ratio and that the crystallization kinetics of these materials is predominantly nucleation driven [6, 7, 8]. On the other hand, the effects of various dopants in eutectic Sb-Te such as Ge, Ga, In, and Ag have been extensively investigated [9]. Furthermore, the performance of Ga-Sb-Te alloys

located on Sb-rich tie-line SbTe-GaSb for phase-change memory have been studied [10].

In such framework, the resistivity-temperature dependence of the 1000 nm Ga-Sb-Te thin films is investigated. Then, we can accomplish and compute the thermal and electrical parameters for under investigated thin films proceeding from the thin films at different heating rates based on their surface resistance as a function of temperature. The amorphous/crystalline nature of the studied as-deposited Ga-Sb-Te thin film at heating rate equals to ($\beta = 5$ K/min), for example, was confirmed by x-ray diffraction (XRD) measurements.

2 Experimental details

Ga-Sb-Te thin films with (1000 nm) were deposited by the usual melt quench technique. Highly pure materials (99.999%) were weighted based on their atomic percentages, using by an electrical balance type (Sartorius) with accuracy ($\pm 10^{-4}$ g) and sealed in an evacuated silica tubes (10^{-5} Torr) and it was heated at 1100 c for 32 hours. During the melt process the tube was frequently rocked to intermix the constituents and to

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increase homogenization of the liquid. The powdered sample were prepared by grinding of the resulting bulk alloy sample in a mortar whereas the thin films of Ga-Sb-Te were prepared onto well-cleaned glass substrate at room temperatures by thermal evaporation technique via high vacuum coating unit (Edward E 306A, UK). In order to obtain resistance-temperature measurements, the electric current at a constant voltage supply was measured against temperature and the phase transition temperature, T_c of the investigated films was deduced. Post deposited Al electrodes in a square geometry (5.0 mm) were used for resistance-temperature measurements, carried out in the running vacuum. The current was measured by a digital picoammeter (DPM-111 Scientific Instruments, Roorkee) and two-point probe method was used for measuring of the electrical properties.

3 Results and discussion

3.1 Resistivity-Temperature dependence, $R_s - T$

Fig. 1 plots the sheet resistance, R_s data versus the temperature of Ga-Sb-Te thin films with (1000 nm) at different heating rates, where ($\beta = 5, 10, 20, 30$ and 40 K/min) in the range (300-673 K). Fig. 1 appears that the values of R_s decrease continuously until an abrupt drop shows at the crystallization temperature, T_c and after this point (as shown in Fig. 1). The mentioned gradient continues until it gets to the highest degree of crystallization, T_p and then the sheet resistance decreases in a continuous behavior after that. In the range (300-510 K), the arrangement of atoms is not clearly changed with temperature, and therefore, the R_s decreases gradually in this temperature range but slowly. In this region, the state of the investigated films is amorphous and the arrangement of atoms is random, causing its high R_s . When the temperature is increased above T_c , the atoms have sufficient energy to rearrange. The arrangement of atoms is ordered such that the films are transformed from amorphous to crystalline state and the R_s rapidly decrease. This is due to the grain growth of the film proceeding as the temperature is increased [11]. The obtained values of T_c and T_p for the studied films are listed in Table 1. The contemplator for the resistivity and the x-ray curves that the x-ray curve supports, with all strength, the sheet resistance curves with respect to the temperature of crystalline transformation.

Now, the first derivation of the resistivity, R_s as a function of the temperature will lead us to know the first pillar of the thermal investigations. Fig. 2 represents the derivative of the sheet resistance, $\frac{dR_s}{dT}$ versus the temperature, T . On the other hand, the exothermic heat flow is given by the posterior relation:

$$\Delta Q_{exo} = -\left[\frac{dR_s}{dT}\right]_{endo}, \quad (1)$$

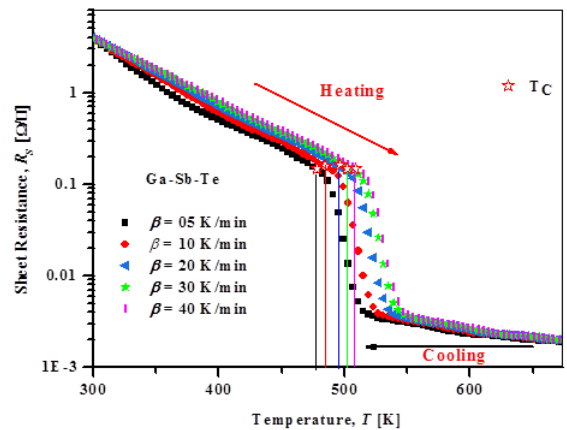


Fig. 1: Relationship between resistivity, (R_s) and temperature, T , for the Ga-Sb-Te thin films at different heating rates.

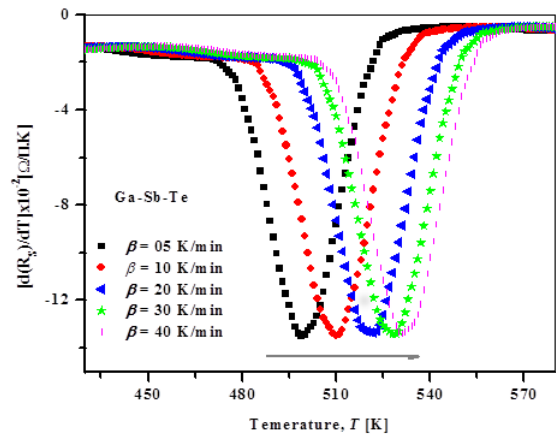


Fig. 2: Relationship between the derivative of sheet resistance, $[dR_s/dT]$ and temperature, T , for the Ga-Sb-Te thin films at different heating rates.

The exothermic heat flow, ΔQ_{exo} against temperature, T , according to Eq. (1) is shown in Fig. 3 for the studied films. This figure elucidates the crystallized fraction, χ_T , at a given temperature T , which given by $\chi_T = A_T/A$ where A is the total area of the exothermic heat flow between the temperature, T_i and T_f . Here, T_i is initial crystallization temperature, T_f is the final crystallization temperature and A_T is the area between T_i and a given temperature, T .

On the other hand, the area under the crystallization peak is directly proportional to the total amount of alloy crystallized. The ratio between the ordinates and the total area of the peak gives the corresponding crystallization rates, which make it possible to plot the curves between the volume crystallization fraction and temperature, T . The graphical representation of the volume crystallized fraction, (χ) appears the typical sigmoid curve as a

Table 1: Maximum crystallization rate $(d\chi/dt)_P$, temperature of crystallization (T_c), peak crystallization temperatures (T_p), kinetic exponent n , and the crystallization activation energy, according to method of Matustia for the Ga-Sb-Te thin films at different heating rates.

β [K/min]	$d\chi/dt \times 10^{-3} (S^{-1})$	T_c	T_p	n	E_c [KJ/mole]	E_c [eV]
5	166.96	478	499.121	2.12762	237.77677	2.46553
10	327.34	484	509.162	2.25863	259.6959	2.69281
20	640.24	495	520.636	2.41479	258.94426	2.68502
30	948.48	503	527.162	2.50674	321.83157	3.3371
40	1253.99	508	531.636	2.57111	366.08832	3.79601
				$\langle n \rangle = 2.376$		

function of temperature at different heating rates for studied thin films as shown in Fig. 4 and given by the subsequent equation:

$$\chi = \sum_{i=0}^s \Delta Q_{exo} / \sum_{i=0}^{99} \Delta Q_{exo}, \tag{2}$$

Where, s is number of points of, (namely, $s = 0$ to 99).

Furthermore, we can obtain the relationship between crystallization rate, $(d\chi/dt)$ and the temperature, T by derivation of the volume crystallized fraction as a function of time and it is given by the subsequent relation:

$$\begin{aligned} \left(\frac{d\chi}{dt}\right) &= \frac{dT}{dt} \times \left(\frac{d\chi}{dT}\right) = \beta \times \left(\frac{d\chi}{dT}\right) \\ \left(\frac{d\chi}{dt}\right)_P &= \frac{dT}{dt} \times \left(\frac{d\chi}{dT}\right)_P = \beta \times \left(\frac{d\chi}{dT}\right)_P = \beta \times T_p \end{aligned} \tag{3}$$

Here, β is the heating rate $(dT/dt)_P$ and is the maximum crystallization rate. Fig. 5 plots of the crystallization rate $(d\chi/dt)$ as a function of temperature, T . The values of the maximum crystallization rate computed according to Eq. (3) and listed in Table 1. From Fig. 4 and Fig. 5, one can infer that the saturation of crystallization shifts towards the higher temperature as the heating rate for the investigated films increases.

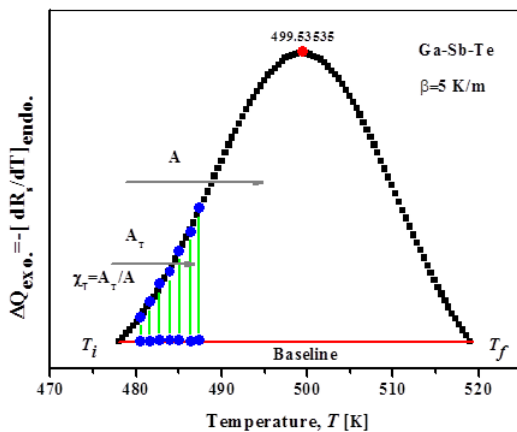


Fig. 3: The exothermic heat flow against temperature for the Ga-Sb-Te thin films at heating rate, $\beta = 5$ K/min.

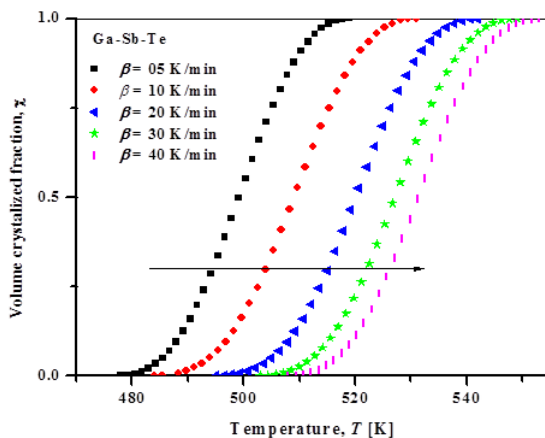


Fig. 4: The crystallization rate, $(d\chi/dt)$ versus temperature, T , for the Ga-Sb-Te thin films at different heating rates.

3.2 Estimation of the activation energy

The activation energy is the minimum energy needed for the reaction to occur, expressed in Joules per mole or Kelvin per mole. In this work, we will address the methods of Kissinger and Matusita to determine the activation energy for the studied film.

3.2.1 Method of Kissinger

There is approach often used to compute kinetic parameters, is called Kissinger's approach [12]. According to this approach, the activation energy, of amorphous-crystalline transformation was originally determining via the following relation [12] as:

$$\ln(\beta/T_p^2) = -E_c/RT_p + \ln(E_c/RK_0) \tag{4}$$

According to Kissinger's approach, the maximum reaction rate occurs at peak temperature, T_p . A plot of $\ln(\beta/T_p^2)$ against $(1000/T_p)$ gives the values of the pre-exponential factor, K_0 and the activation energy, $\ln(\beta/T_p^2)$. Fig. 6 plots of E_c versus $(1000/T_p)$ for the studied thin films. The activation energy, E_c and frequency factor, K_0 , are computed by least squares fitting method. Namely, from the slope and the intercept of the straight lines in the plots, the values of the activation energy and the pre-exponential factor, K_0 were obtained and these values equal to 131.32 KJ/mole, that equals to (1.36 eV), and 1.42×10^{-8} , respectively [13,14].

The general kinetic description of a reaction is based on several assumptions and the most important of these assumptions is the temperature dependence of the reaction rate constant, $K(T)$ that is described by the Arrhenius equation as follows;

$$K(T_p) = K_0 \exp\left[-\frac{E_c}{RT_p}\right] \quad (5)$$

the value of this criterion allusive the tendency of glass to devitrify on heating, whereas the glass formation is a kinetic process. The, $K(T_p)$, as a function of T_p for the studied system is shown in Fig. 6.

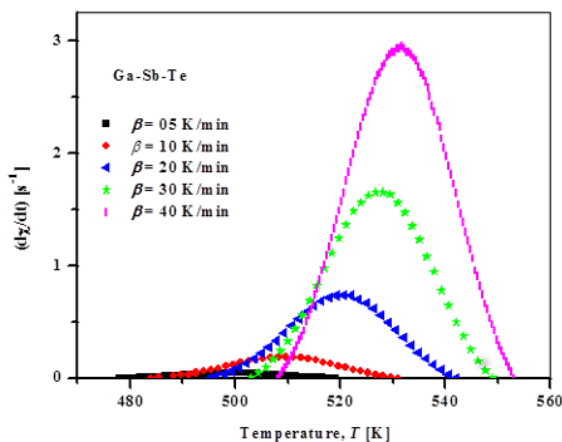


Fig. 5: The typical sigmoid curve of the volume crystallized fraction, χ , as a function of temperature, T , for the Ga-Sb-Te thin films at different heating rates.

Now, the kinetic exponent, n computed using by the following equation:

$$n = \frac{(d\chi/dt)_P \times RT_p^2}{(0.37\beta E_c)} \quad (6)$$

The determined values of n for the investigated thin films are tabulated in Table 1. As well, the experimental values of the peak crystallization temperature T_p are listed in Table 1. The kinetic exponent, n was computed based

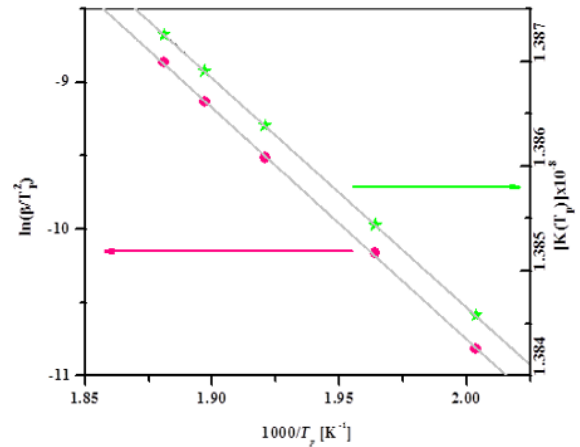


Fig. 6: The plot both of $\ln(\beta/T_p^2)$ and $K(T_p)$ versus $1000/T_p$ for the Ga-Sb-Te thin films at different heating rates.

on the mechanism of crystallization Mahadevan et al. [15] have appeared that n may be 4, 3, 2, which are related to different glass-crystal transformation mechanisms: $n = 4$, volume nucleation, three-dimensional growth; $n = 3$, volume nucleation, two-dimensional growth; $n = 2$, volume nucleation, one-dimensional growth; $n = 1$, surface nucleation, one-dimensional growth from surface to the inside. Therefore, bearing in mind, the above obtained mean values for crystallization region (as shown in Table 1) means volume nucleation, one-dimensional growth because values is integer, namely, $m = n - 1 = 1$. The computed n values are not integers. This means that the crystallization occurs by more than one mechanism [16, 17, 18, 19, 20].

3.2.2 Method of Matusita

Matusita model evidences the importance of the factor, m for the determination of the activation energy of the crystallization process. This fact is related to the nucleation and growth of the crystallites in the amorphous matrix. Furthermore, the activation energy of the studied thin films was deduced by the Matustia equation [18, 21, 22, 23]:

$$\ln(-\ln(1 - \chi)) = n \ln \beta - 1.052 \frac{m E_c}{RT} + const. \quad (7)$$

Where, $(m = n - 1)$ is the dimension order parameter and (n) is constant related to the crystallization mechanism as mentioned above. Plots of $\ln(-\ln(1 - \chi))$ versus $(1000/T)$ for the investigated thin films at different heating rates are appeared in Fig. 7. For the computation of E_c we take into consideration the linear region of this plot. From the average, n values and $m E_c$, $(n = m + 1)$, the effective activation energies E_c for the studied thin films are computed and listed in Table 1.

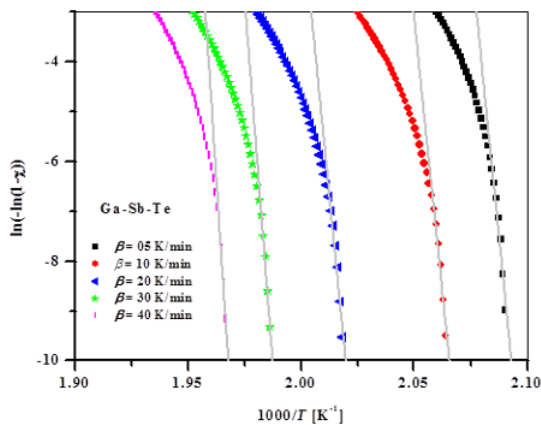


Fig. 7: The plot of $\ln(-\ln(1-\chi))$ versus $(1000/T)$ for the Ga-Sb-Te thin films at different heating rates.

4 Identification of the crystalline phases

The amorphous/crystalline nature of the studied as-deposited Ga-Sb-Te thin film at heating rate equals to ($\beta = 5$ K/min), for example, was confirmed by x-ray diffraction (XRD) measurements as presented in Fig. 8. The absence of any peak in the XRD scan of the investigated film confirms its amorphous nature. But, the diffractogram of an annealed film at $T_C = 478$ K, [$T_C < T = 485$ K $> T_p$] and $T_p = 499.12$ K shows sharp peaks as presented in Fig. 8. These sharp peaks indicate the development of amorphous structure along with poly-crystalline phases during the heat treatment of studied films. X-ray pattern only appears two crystalline phase when the film reaches either $T = 485$ K or ($T = T_p$) = 499.12 K (both after the crystallization temperature, $T_C = 478$ K) at the studied heating rate, ($\beta = 5$ K/min). The diffraction of dominant peaks were indexed with Gallium-Antimony-Telluride phase [No. card: (1-89-3665)] and Antimony-Gallium phase [No. card: (7-215)] along their respective 2θ value as presented in Fig. 8.

5 Conclusions

The studied thin films at different heating rates were prepared by thermal evaporation technique. Temperature dependence of electrical resistance $R_s - T$ of the Ga-Sb-Te films has one sharp transition at about 478, 484, 495, 503 and 508 K for the five heating rates. This transformation is associated with a transition between amorphous and crystalline states. Then, the experimental of the thermal and electrical properties of thermally evaporated thin films (1000 nm) of the Ga-Sb-Te have been predestined and discussed based on sheet resistance, R_s measurements. Thus, the thermal properties and kinetics parameters such the activation energy of amorphous-crystalline transformation E_c the Avrami

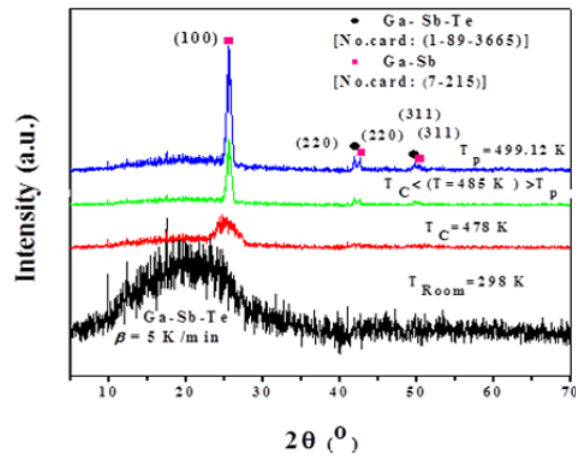


Fig. 8: X-ray diffraction patterns of the Ga-Sb-Te thin films at different temperatures with heating rate, $\beta = 5$ K/min.

exponent n , the frequency factor, K_0 , have been computed. Finally, several of electrical parameters have been computed. One of the most important of these parameters is the activation energy that has the same behavior of pre-exponential factor in any region. The amorphous/crystalline nature of the studied as-deposited Ga-Sb-Te thin film at heating rate equals to ($\beta = 5$ K/min), for example, was confirmed by x-ray diffraction (XRD) measurements.

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