1. Introduction

Phase-change memory technology is based on the high speed reversible amorphous-to-crystalline transformation of a thin film material. The limiting process in rewritable media is the slow crystallization process. For this reason, in recent years many experimental and theoretical studies to investigate the amorphous-to-crystalline phase transformation have appeared in the literature.

Studies of crystallization kinetics of phase change films, are often analyzed using the Johnson–Mehl–Avrami-Kolmogorov (JMAK) model for isothermal annealing (see for example ref. [1-5]), which allows to determine the activation energy for the crystallization process. According to the JMAK model the transformed volume fraction $x$ can be determined by the following expression:

$$ x = 1 - \exp(-Kr^n), $$

where $K = \gamma \exp(-E/kT)$ and $\gamma$, $E$, $t$ and $n$ are the frequency factor, effective activation energy, time of annealing and Avrami exponent, respectively. In materials with random nucleation and isotropic growth the plot $\ln(-\ln(1 - x))$ vs $\ln(t)$ should be a straight line with a slope corresponding to the Avrami exponent, which provides information about the mechanisms of crystallization.

The kinetic parameters in the literature for stoichiometric $\text{Ge}_2\text{Sb}_2\text{Te}_5$, $\text{Ge}_4\text{Sb}_2\text{Te}_4$ and $\text{Ge}_4\text{Sb}_7\text{Te}_5$
(the most common material used in phase change technology) show a large discrepancy. Values from 1.2 to 4.4 for the Avrami exponent and from 0.81 to 4.3 eV for the effective activation energy have been reported [1-7]. To our knowledge the kinetic parameters of Sb:Te eutectic doped by Ge have not been reported in the literature.

The aim of this work is to compare the isothermal crystallization kinetics in the films having both the Ge:Sb:Te stoichiometric compositions and Ge-doped Sb:Te near the eutectic point, with the Sb$_{65}$Te$_{35}$ composition.

2. Experimental procedures

The stoichiometric amorphous Ge$_2$Sb$_2$Te$_5$, Ge$_5$Sb$_2$Te$_4$ and Ge$_4$Sb$_5$Te$_5$ films, with thickness between 150-300 nm, were produced using DC magnetron sputtering. The composition of films was evaluated by energy dispersive spectroscopy (EDS) and it did not differ more than 1-2% from the composition of the sputtering targets. Sb:Te eutectic films with 2, 5 and 10 atomic percent of Ge were prepared by thermal evaporation of the bulk alloys onto corning glass substrates. The chemical compositions of films determined by EDS were Sb$_{70}$Te$_{30}$, Ge$_2$Sb$_{70}$Te$_{28}$, Ge$_5$Sb$_{70}$Te$_{25}$ and Ge$_{10}$Sb$_{65}$Te$_{25}$.

In situ optical reflection (using a laser diode emitting at 650 nm) and X-ray measurements were carried out using a resistance heater. The temperature was controlled with a device which was programmed to heat the sample to a predetermined temperature for isothermal measurements. X-ray diffraction measurements were carried out using a Rigaku X-ray diffractometer with a Cu tube.

In the reflectance measurements the volume fraction of crystalline phase was calculated using the generally employed assumption that the signals are linearly related to the transformed crystalline volume fractions $x$ using the expression [1, 8]:

$$x = \frac{R(t) - Ra}{Rc - Ra},$$

where $Ra$ and $Rc$ are the reflectance of amorphous and crystalline phase, respectively.

3. Results and discussion

Figures 1, 2 and 3 show the evolution of the volume fraction of the transformed crystalline phase obtained from reflectance measurements during isothermal annealing at the indicated temperatures in films with the following compositions: Ge$_2$Sb$_2$Te$_5$ (figure 1a), Ge$_5$Sb$_2$Te$_4$ (figure 2a) and Sb:Te eutectic doped with 5 at. % of Ge (figure 3a). All films show long incubation time for crystallization, namely, the annealing time required to reach a critical nuclei size or to observe an abrupt increase in the crystalline volume fraction [9]. However, there are two well defined crystallizations patterns; in films with the Ge$_2$Sb$_2$Te$_5$ and Ge$_5$Sb$_2$Te$_4$ (not shown) compositions, the results show a relative large amounts of crystallized phase (about 20%) during the incubation time, whereas in those with the other five compositions the crystallized material during this time is much smaller (less than 2%).

X-ray measurements indicate that during incubation time, a metastable phase with the fcc stoichiometric Ge$_4$Sb$_4$Te$_7$ composition is formed in the Ge$_2$Sb$_2$Te$_5$ and Ge$_5$Sb$_2$Te$_4$ films. This metastable phase has a lower crystallization temperature and it probably appears in the two stoichiometric ternary alloys due to local fluctuations in the composition of the amorphous films [10, 11]. Thus, the process of isothermal crystallization in Ge$_2$Sb$_2$Te$_5$ and Ge$_5$Sb$_2$Te$_4$ takes place in two stages: in the first stage, nuclei of a metastable phase with composition Ge$_4$Sb$_4$Te$_7$ precede the formation of the stable fcc phases; in the second stage, the nuclei transform into the equilibrium fcc stoichiometric structures with a composition corresponding to the parent amorphous material.

In materials where a phase transformation starts with the formation of metastable phases, the isothermal crystallization process cannot be simply described by the JMAK theory and the Avrami plots are not linear which implies that the Avrami exponent $n$ does not remain constant during the crystallization process (figure 1b). The kinetics of the two-stage crystallization can be described by a modified JMAK model which assumes that the metastable phase grows up to a certain fraction and then stops growing. The second stage consists of simultaneous nucleation and growth of the stable phase into the metastable (until the grain limit is reached) and within the amorphous phases [10, 11].
The dependencies of volume fraction (a) and an Avrami plot (b) for a Ge$_2$Sb$_2$Te$_5$ film obtained from reflection measurements (points), results of simulations using the model with metastable phase formation are the continuous lines. The proposed model allows simulating the kinetics of complex crystallization processes such as the one shown in figure 1b. The model predicts three crystallization stages identified by different slopes: the first (at short annealing times) corresponding to the formation of the metastable phase, the second one with a small slope (at intermediate annealing times) corresponding to a stage between metastable and the stable phases and the final stage corresponding to the formation of the fcc phase with the same composition as the amorphous films.

In films with compositions different than Ge$_2$Sb$_2$Te$_5$ and Ge$_1$Sb$_2$Te$_4$, the X-ray diffraction data shows crystallization into the same and final phase during the whole annealing time. In this case it is possible to neglect the amount of crystallized material during the incubation time $\tau$ and define $\tau$ as the beginning of the transformation [1], the JMAK equation is now expressed:

$$x = 1 - \exp[-K(t - \tau)^n]$$  \hspace{1cm} (3)

According to equation (3) the plot $ln(-ln(1 - x))$ vs $ln(t-\tau)$ must be a straight line with the slope $n$ (figures 2b and 3b). The value of $n$ for Ge$_2$Sb$_2$Te$_5$ was about 1.8 which according to [12] corresponds to a diffusion controlled growth from small dimension grains with decreasing nucleation rate. Additionally, the calculated effective activation energy, determined from the Avrami plot for different temperatures using the Arrhenius type relation for $K$, was $3.46 \pm 0.22$ eV, in good agreement with other values reported in the literature ($3.48 \pm 0.12$ eV) obtained using the Kissinger analysis [13].

Figure 1. The dependencies of volume fraction (a) and an Avrami plot (b) for a Ge$_2$Sb$_2$Te$_5$ film obtained from reflection measurements (points), results of simulations using the model with metastable phase formation are the continuous lines.

For the Sb:Te eutectic undoped and doped with 2, 5 and 10 at. % Ge (figure 3), the results of measurements analyzed using equation (3) provided values of the Avrami exponent $n$ slightly dependent on the Ge content and are in the range of 1.25-1.45. According to [13] the values of $n$ in the range $1 < n < 1.5$ correspond to a crystallization process dominated by growth of particles with appreciable initial volume. The effective activation energy of crystallization in those films shows a
clear increase from 2.0 eV in the undoped Sb\textsubscript{70}Te\textsubscript{30} films to 2.6 eV in films doped with 10 at % Ge. This effect can be related to the increase in the number and the strength of the chemical bonds in the amorphous state generated by the introduction of an element with higher coordination number such as Ge.

![Figure 3](image)

**Figure 3.** The dependencies of volume fraction (a) and an Avrami plot (b) for a Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} film obtained from reflection measurements (points), the results of fitting using JMAK models are the continuous lines.

### 4. Conclusion

In this work the crystallization mechanism in phase-change materials with different compositions is compared. The traditional JMAK model did not explain the isothermal crystallization kinetics results in all samples. In Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} and Ge\textsubscript{1}Sb\textsubscript{2}Te\textsubscript{4} films crystallization starts with formation of a metastable phase, vanishing after certain annealing time. The disappearance of this phase is associated with the formation of the final fcc phase, inside the metastable grains and in the remaining amorphous material. In the Ge\textsubscript{4}Sb\textsubscript{1}Te\textsubscript{5}, the undoped and the Ge-doped Sb:Te eutectics films crystallization kinetics can be described by a JMAK model which take into account incubation times. The highest effective activation energy therefore the best thermal stability among the studied phase-change material corresponded to the Ge\textsubscript{4}Sb\textsubscript{1}Te\textsubscript{5} films.

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