

# Estimate of the Crystallization Kinetics in Stoichiometry Compositions Films of Ge:Sb:Te

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## ABSTRACT

The aim of this work is to compare the isothermal crystallization kinetic in the films along GeTe-Sb<sub>2</sub>Te<sub>3</sub> line with composition Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>, Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub>, Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> and Ge<sub>4</sub>Sb<sub>1</sub>Te<sub>5</sub> using mainly Johnson-Mehl-Avrami-Kolmogorov (JMAK) model. Results obtained have shown different crystallization mechanism in the investigated films. In Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> and Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> films the analysis of the kinetic results (Avrami coefficient) showed that at the beginning of crystallization a metastable phase appeared with the Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> composition, this is followed by the nucleation and growth of the stable fcc phase up to full crystallization. In contrast Ge<sub>4</sub>Sb<sub>1</sub>Te<sub>5</sub> and Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> films show diffusion control growing from small dimension grains with decreasing nucleation rate.

**Keywords:** Crystallization; Ge:Sb:Te; JMAK Model

## 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 that 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 the following reference [1-5]), which allow 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.

$$x = 1 - \exp(-Kt^n) \quad (1)$$

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 Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>, Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub>, Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> and Ge<sub>4</sub>Sb<sub>1</sub>Te<sub>5</sub> (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].

The aim of this work is to compare the isothermal crystallization kinetic in the films along GeTe-Sb<sub>2</sub>Te<sub>3</sub> line.

## 2. Methodology

The amorphous Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>, Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub>, Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> and Ge<sub>4</sub>Sb<sub>1</sub>Te<sub>5</sub> films, with thickness about of 200 nm, were produced using thermal evaporation from bulk alloys. The composition of films was evaluated by energy dispersive spectroscopy (EDS) and it did not differ more than 2% from the composition of the bulk materials.

*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 em-

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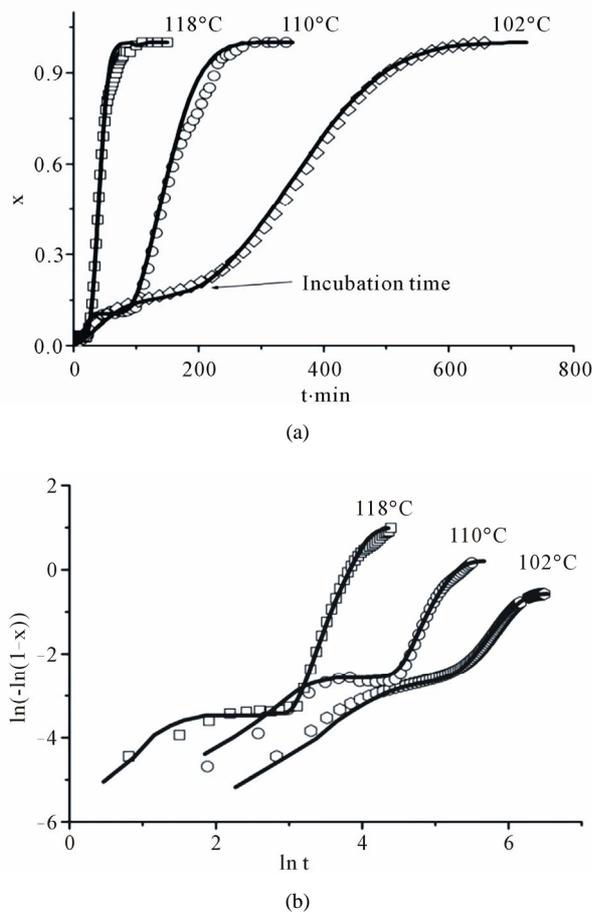
ployed assumption that the signals are linearly related to the transformed crystalline volume fractions  $x$  using the next expression.

$$x = \{R(t) - Ra\} / \{Rc - Ra\} \quad (2)$$

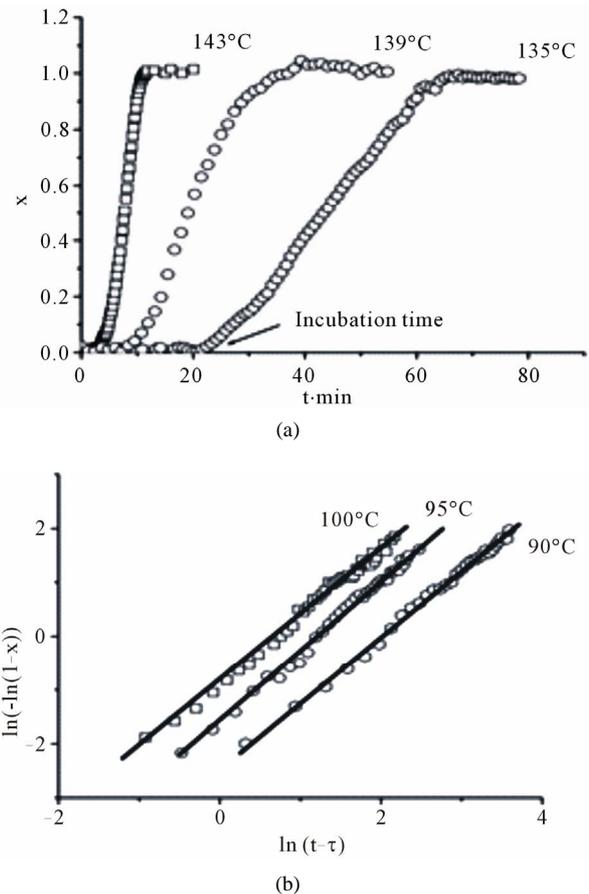
where  $Ra$  and  $Rc$  are the reflectance of amorphous and crystalline phase, respectively.

### 3. Results and Discussion

The next **Figure 1** and **Figure 2**, show the evolution in 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:  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ , **Figure 1(a)**, and  $\text{Ge}_4\text{Sb}_1\text{Te}_5$ , **Figure 2(a)**. All films show long incubation time for crystallization, or time required to reach a critical nuclei size which lead to an abrupt increasing in the crystalline volume fraction. However there are two well defined crystallizations behaviors; in films with the



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



**Figure 2.** The dependencies of volume fraction (a) and Avrami plot (b) for a  $\text{Ge}_4\text{Sb}_1\text{Te}_5$  film obtained from reflection measurements (points), the results of fitting using JMAK models are the continuous lines.

$\text{Ge}_2\text{Sb}_2\text{Te}_5$  and  $\text{Ge}_1\text{Sb}_2\text{Te}_4$  (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 two compositions ( $\text{Ge}_1\text{Sb}_4\text{Te}_7$  and  $\text{Ge}_4\text{Sb}_1\text{Te}_5$ ) 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  $\text{Ge}_1\text{Sb}_4\text{Te}_7$  composition is formed in the  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  and  $\text{Ge}_1\text{Sb}_2\text{Te}_4$  films. This metastable phase has a lower crystallization temperature and it probably appears in the two ternary alloys due to local fluctuations in the composition of the amorphous films [8,9]. Thus, the process of isothermal crystallization in  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  and  $\text{Ge}_1\text{Sb}_2\text{Te}_4$  takes place in two stages: in the first stage, nuclei of a metastable phase with composition  $\text{Ge}_1\text{Sb}_4\text{Te}_7$  precede the formation of the stable fcc phases; in the second stage, the nuclei transform into the equilibrium fcc stoichiometric structures with a composition correspondent to the parent amorphous material.

In materials where 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 Avrami exponent  $n$  does not remain constant during the crystallization process (**Figure 1(b)**). The kinetics of 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 [8,9].

In films with compositions  $\text{Ge}_4\text{Sb}_1\text{Te}_5$  and  $\text{Ge}_1\text{Sb}_4\text{Te}_7$ , 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:

$$x = 1 - \exp\left[-K(t - \tau)^n\right] \quad (3)$$

According to Equation (3) the plot  $\ln(-\ln(1-x))$  vs  $\ln(t - \tau)$  must be a straight line with the slope  $n$  (**Figure 2(b)**). This means that crystallization process in  $\text{Ge}_4\text{Sb}_1\text{Te}_5$  and  $\text{Ge}_1\text{Sb}_4\text{Te}_7$  material display random nucleation and isotropic growth.

The values of Avrami exponent  $n$  ( $n = 1.8$  for  $\text{Ge}_4\text{Sb}_1\text{Te}_5$  and  $n = 1.94$  for  $\text{Ge}_1\text{Sb}_4\text{Te}_7$ ) and effective activation energy  $E_a$  ( $E_a = 3.46$  eV for  $\text{Ge}_4\text{Sb}_1\text{Te}_5$  and  $E_a = 1.7$  eV for  $\text{Ge}_1\text{Sb}_4\text{Te}_7$ ) have been calculated from reflection measurements. According to J. W. Christian [10], the values of  $n$  in the range  $1.5 < n < 2.5$  correspond to a crystallization process dominated by all shapes growing from small dimensions with decreasing nucleation rate.

Relative low effective activation energy obtained for  $\text{Ge}_1\text{Sb}_4\text{Te}_7$ , low crystallization temperature, and the possibility to growth from small dimension allow suggesting that the appearance of nanocrystalline nuclei with the  $\text{Ge}_1\text{Sb}_4\text{Te}_7$  phase in the process of crystallization of the  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  and  $\text{Ge}_1\text{Sb}_2\text{Te}_4$  materials could be related to local fluctuations in composition of the amorphous matrix.

#### 4. Conclusion

In this work the crystallization mechanism in phase-change materials along  $\text{GeTe-Sb}_2\text{Te}_3$  line is compared. The traditional JMAK model did not explain the isothermal crystallization kinetics results in all samples. In  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  and  $\text{Ge}_1\text{Sb}_2\text{Te}_4$  films crystallization starts with

formation of a metastable phase with  $\text{Ge}_1\text{Sb}_4\text{Te}_7$  composition. In contrast in  $\text{Ge}_1\text{Sb}_4\text{Te}_7$  and  $\text{Ge}_4\text{Sb}_1\text{Te}_5$  crystallization kinetics can be described by a JMAK model which take into account incubation times

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