Study of Crystallization Kinetics in GeSbTeSeM (M=Cu, Co, Ni, Pb) Phase Change Materials

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Abstract- We obtained the experimental exothermal curves of chalcogenide alloys Ge_{x}Sb_{y}Te_{z}Se_{t}M_{1.5}, M=Co, Cu, Ni, Pb, and applied the Kissinger’s formula to extract the activation energy \( E_c \). Our results indicate that the activation energy \( E_c \) increases while doping a small amount of M metals. At isothermal electrical resistivity measurement, the resistivity of the sputtered doped films decreases with time. Also the viscosity decrease rate (dR/dt) increases with the increase of isothermal temperature. This phenomenon is due to phase transition between amorphous and crystalline states. The crystallization process in our study is interpreted successfully by Johnson-Mehl-Avrami (JMA) transformation equation, and the crystallization time \( \tau \) is extracted from the JMA equation when we compared the experimental results to the equation. We find that the crystallization time for Ge_{x}Sb_{y}Te_{z}Se_{t} alloy with doping M is shorter significantly than that for Ge_{x}Sb_{y}Te_{z}Se_{t}, alloy without doping, and it is lower than 50 ns at 730 K and near 100 ns, respectively. These results indicate that the M dopant enhances crystallization process.

Key words: crystallization time, phase change material, phase-change disk

1. Introduction

In recent years there is a growing interest in both theoretical and practical researches about the phase change materials. The crystallography state of the recording media switches between crystalline and amorphous solids induced by a laser beam. The recorded data is distinguished by the reflectivity differences between crystalline and amorphous solids. In practical, it is difficult to erase a written spot within several hundred nanoseconds if the amorphous to crystalline transition rate of the material is not sufficiently high. For this reason, the studies of crystallization rate and the factors that influence it are very important for the development of new kinds of phase change materials. Many experiments were conducted and focused on the chalcogenide alloys in this decade because of their rewritable capabilities. The research topics are mainly included: to decrease the crystallization time, to reduce the crystallization temperature, to decrease the melting point, to increase the activation energy and to form the compatible alloys or compounds. In this paper, we focus on the calorimetric studies of chalcogenide alloys Ge_{x}Sb_{y}Te_{z}Se_{t}M_{1.5} to understand the crystallization mechanism. We further investigate the activation energy \( E_c \) which is the energy barrier of phase transition between amorphous solid and crystalline solids. Crystallization rate is also important for amorphous solid to crystalline solid transformation and it has a direct influence on the overwriting quality of phase-change disk. Our object is to find the effect of \( E_c \) and \( \tau \) on the write/erase of phase change media.

2. Experiment

Five alloys of Ge_{x}Sb_{y}Te_{z}Se_{t}Cu, Ge_{x}Sb_{y}Te_{z}Se_{t}Co_{1.5}, Ge_{x}Sb_{y}Te_{z}Se_{t}Ni_{1.5}, and Ge_{x}Sb_{y}Te_{z}Se_{t}Pb_{1.5} are prepared from the highly pure elements. First the mixtures sealed in vacuum are heated at 850°C for five hours by a rotating furnace. The Ge_{x}Sb_{y}Te_{z}Se_{t}M_{1.5} alloy ingots are thoroughly pulverized, ground and hot-pressed to two-inch diameter sputtering target. Thin films (the samples which we measure in this study) of these alloys are prepared by RF sputtering, keeping the substrates at room temperature with a working pressure of about 3 mbar. The amorphous nature of these films is verified by the X-ray diffraction. The crystallization experiments are performed in a differential scanning calorimeter. The exothermal curves obtained at different heating rates (from 5 to 80 K/min) are used to investigate the crystallization kinetics of Ge_{x}Sb_{y}Te_{z}Se_{t}M_{1.5} amorphous. Dc resistances were measured using the standard four-probe technique, using a Lakeshore 120 current source and a keithley 2182 nanovoltmeter. Isothermal resistance measurements were performed in a tube furnace in an argon atmosphere. The time dependence resistances at various measuring temperatures for each sample were compared with Johnson-Mehl-Avrami (JMA) equation to extract the crystallization time. For the measurements, the sample resistances were continuously monitored by a personal-computer-based data-acquisition system.

3. Results and Discussion

The activation energy \( E_c \) of a material indicates that the energy barrier of a material must be overcome during its amorphous-to-crystalline transformation. The activation energy \( E_c \) was calculated using the equation derived by Kissinger.
Fig. 1 The $\ln(\alpha/T_p^2)$ as a function of reciprocal crystallization peak temperature $1/T_p$ for our samples. The symbols are the experimental data and the solid lines are guide to the eye where solid circles, solid squares, open squares, open rhombus and open circles are for Ge$_{0.8}$Sb$_{0.2}$Te$_{0.8}$Se$_{0.2}$, Ge$_{0.8}$Sb$_{0.2}$Te$_{0.8}$Se$_{0.2}$Cu$_{0.1}$, Ge$_{0.8}$Sb$_{0.2}$Te$_{0.8}$Se$_{0.2}$Co$_{0.1}$, Ge$_{0.8}$Sb$_{0.2}$Te$_{0.8}$Se$_{0.2}$Ni$_{0.1}$, and Ge$_{0.8}$Sb$_{0.2}$Te$_{0.8}$Se$_{0.2}$Pb$_{0.1}$, respectively.

$$\ln(\alpha/T_p^2) = -E_c/RT_p + \text{const}$$  (1)

where $\alpha$, $T_p$, and $R$ are respectively referred to the heating rate, crystallization peak temperature and gas constant. The experimental exothermal curves of our samples were measured between 320 and 870 K. Figure 1 shows the $\ln(\alpha/T_p^2)$ as a function of reciprocal crystallization peak temperature $1/T_p$ for our samples. Obviously, our results are satisfactorily described by Kissinger's formula. The activation energies $E_c$ are extracted to be 3.29, 3.87, 3.47, 3.37, and 3.34 ev for samples Ge$_{0.8}$Sb$_{0.2}$Te$_{0.8}$Se$_{0.2}$, Ge$_{0.8}$Sb$_{0.2}$Te$_{0.8}$Se$_{0.2}$Cu$_{0.1}$, Ge$_{0.8}$Sb$_{0.2}$Te$_{0.8}$Se$_{0.2}$Co$_{0.1}$, Ge$_{0.8}$Sb$_{0.2}$Te$_{0.8}$Se$_{0.2}$Ni$_{0.1}$, and Ge$_{0.8}$Sb$_{0.2}$Te$_{0.8}$Se$_{0.2}$Pb$_{0.1}$, respectively. Our results indicate that a small amount of doped M can raise activation energy $E_c$.

During the isothermal transformation, the extent of crystallization ($X$) of a certain material is represented by Avrami equation as

$$X(t) = 1 - \exp[-(t/\tau)^\kappa]$$  (2)

where $\kappa$ is a parameter related to the mode of transformation. Empirically, at temperatures below the melting point the characteristic time is described by the Arrhenius expression: $\tau = \tau_c \exp (E_c/k_B T)$ where $E_c$ is the activation energy. To facilitate a quantitative comparison with experimental result, we rewrite Eq.(2) in the following form:

$$\ln t = 1/\kappa \ln [\ln(1-X)^{-1}]+\ln \tau$$  (3)

Phase transformations from amorphous to crystalline often result in change in electrical resistivity. Assuming a linear relation between the instantaneous value of resistivity, $\rho(t)$, and the volume fraction of the isothermally transformed material $X(t)$, the latter can be determined from $X(t) = [\rho - \rho(t)] / [\rho - \rho_\infty]$ where $\rho_\infty$ and $\rho$ are the resistivity of the initial phase a and the transformed phase c, respectively.

Figure 2 shows the measured, normalized resistivities $\rho(t)/\rho_\infty$ as a function of time for a representative film, Ge$_{0.8}$Sb$_{0.2}$Te$_{0.8}$Se$_{0.2}$Ni$_{0.1}$, at four measuring temperatures of (from right to left) 440, 445, 450, and 452 K.

The plot of $\ln\ln(1/(1-X))$ vs. ln(time in seconds) is shown in Fig.3 for five representative Ge$_{0.8}$Sb$_{0.2}$Te$_{0.8}$Se$_{0.2}$M$_{0.1}$ alloys with Ge$_{0.8}$Sb$_{0.2}$Te$_{0.8}$Se$_{0.2}$ (at 452 K, solid circles), Ge$_{0.8}$Sb$_{0.2}$Te$_{0.8}$Se$_{0.2}$Co$_{0.1}$ (at 459 K, open squares), Ge$_{0.8}$Sb$_{0.2}$Te$_{0.8}$Se$_{0.2}$Cu$_{0.1}$ (at 452 K, open rhombus), Ge$_{0.8}$Sb$_{0.2}$Te$_{0.8}$Se$_{0.2}$Ni$_{0.1}$ (at 452 K, open squares), Ge$_{0.8}$Sb$_{0.2}$Te$_{0.8}$Se$_{0.2}$Pb$_{0.1}$ (at 452 K, open circles), respectively. It is clearly seen that the experimental data for each composition film follows a linear behavior, where the slope provides the reciprocal exponent $n$ as described above for the JMA model (Eq.3). Solid line is
The plot of ln ln[1/(1-x)] vs. ln(time in seconds) for five representative Ge$_{0.1}$Sb$_{0.9}$Te$_{0.3}$S$_{0.7}$ alloys with Ge$_{0.1}$Sb$_{0.9}$Te$_{0.3}$S$_{0.7}$ alloys with Ge$_{0.1}$Sb$_{0.9}$Te$_{0.3}$S$_{0.7}$ (at 452 K, solid circles), Ge$_{0.1}$Sb$_{0.9}$Te$_{0.3}$S$_{0.7}$Co$_{0.1}$ (at 459 K, open squares), Ge$_{0.1}$Sb$_{0.9}$Te$_{0.3}$S$_{0.7}$Ni$_{0.1}$ (at 452 K, open rhombus), Ge$_{0.1}$Sb$_{0.9}$Te$_{0.3}$S$_{0.7}$Cu$_{0.1}$ (at 452 K, solid squares), Ge$_{0.1}$Sb$_{0.9}$Te$_{0.3}$S$_{0.7}$Pb$_{0.1}$ (at 452 K, open circles), respectively.

The variation of the crystallization time with reciprocal temperature for Ge$_{0.1}$Sb$_{0.9}$Te$_{0.3}$S$_{0.7}$ (●), Ge$_{0.1}$Sb$_{0.9}$Te$_{0.3}$S$_{0.7}$Cu$_{0.1}$ (■), Ge$_{0.1}$Sb$_{0.9}$Te$_{0.3}$S$_{0.7}$Co$_{0.1}$ (□), Ge$_{0.1}$Sb$_{0.9}$Te$_{0.3}$S$_{0.7}$Ni$_{0.1}$ (○) phase change alloys respectively.

Figure 4 shows the variation of the crystallization time with reciprocal temperature for Ge$_{0.1}$Sb$_{0.9}$Te$_{0.3}$S$_{0.7}$ (●), Ge$_{0.1}$Sb$_{0.9}$Te$_{0.3}$S$_{0.7}$Co$_{0.1}$ (□), Ge$_{0.1}$Sb$_{0.9}$Te$_{0.3}$S$_{0.7}$Ni$_{0.1}$ (○), Ge$_{0.1}$Sb$_{0.9}$Te$_{0.3}$S$_{0.7}$Cu$_{0.1}$ (○) phase change alloys respectively. The linear-fitted solid curve is described by ln τ = 39.1(1000/T) - 69.8 (in sec.) for Ge$_{0.1}$Sb$_{0.9}$Te$_{0.3}$S$_{0.7}$ and ln τ = 31.3(1000/T) - 60.1 for Ge$_{0.1}$Sb$_{0.9}$Te$_{0.3}$S$_{0.7}$M$_{0.1}$ samples. Thus, a dependence τ ≈ e$^{-AT}$ is unambiguously observed. By using linear-fitted results, we obtain the crystallization time τ ~90 and 35 ns for no-doping and doping samples at 730 K. From the observation of Fig.4, we can find the crystallization rate for the sample of Ge$_{0.1}$Sb$_{0.9}$Te$_{0.3}$S$_{0.7}$ is faster than that for no-doping sample, that is Ge$_{0.1}$Sb$_{0.9}$Te$_{0.3}$S$_{0.7}$. (On the same temperature, comparing with M doped samples, the crystallization time (Y axis) of Ge$_{0.1}$Sb$_{0.9}$Te$_{0.3}$S$_{0.7}$ (solid circles) is long.) It is implied that a small amount of M is effective to nucleation. In other word, a small amount of doped M can accelerate the transformation rate for the phase-change switching between amorphous and crystalline states due to enhancement of nucleation process.

In summary, we compared the Kissinger's formula and exothermic curves to extract $E_c$. Our results indicate that Doping a small amount of M in chalcogenide alloys can raise $E_c$ and assist nucleation, i.e. can assist the amorphous to crystalline transformation. We find that doping M can enhance the crystallization rate for Ge$_{0.1}$Sb$_{0.9}$Te$_{0.3}$S$_{0.7}$ alloy.

References


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8) Cleva W. Ow-Yang, Doren Spinner, Yozo Shigesato, david, and C. paine,