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Thickness Dependent Nano-Crystallization in $Ge_2Sb_2Te_5$ films and Its Effect on Devices

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1. Introduction

Phase Change Random Access Memory (PCRAM) is based on electrical induced thermal phase change. It is believed to be the best candidature for next generation non-volatile memory. When the memory size is reduced to nano-scale, nano-crystallization becomes a critical issue. Recently, line-type PCRAM attracts lot of attention because of its simple structure and manufacture process.[1]

In this paper, the fundamental properties of thickenss dependent nano-crystallization in ultra-thin $Ge_2Sb_2Te_5$ films were studied by in-situ exothermal and isothermal electrical resistivity measurements. The crystallization kinetics including the crystallization mechanism, the corresponding activation barrier and the Avrami coefficient was investigated. In addition, the effect of this nano- crystallization on different memory devices was analyzed.

2. Experiments and Results

Samples

Thin $Ge_2Sb_2Te_5$ films were deposited by BLOZER dc magnetron sputtering using a stoichiometric target. GST films of different thickness (30nm, 20 nm, 15 nm, 10 nm, 5 nm) sandwiched by 50 nm ZnS-SiO2 films were prepared. Two 100 nm TiW electrodes were embedded in the GST film for the resistance measurement. The sample was uniformly heated by MicromanipulatorTM H-1000 thermal Chuck System.

Experiments & results

The exothermal measurement (ETTM) was carried on at a heating rate of 0.5 ˚C /min, 1 ˚C /min, 3 ˚C /min, 10 ˚C /min and 20 ˚C /min from 21 ˚C to 220 ˚C. The resistivity dependence on temperature of 30 nm and 5 nm thin films was shown in Fig. 1. The crystallization process can be characterized by the steep resistivity change; therefore it is obvious that the crystallization was delayed when the heating rate increases and this delay in 5 nm GST film is less than the delay in 30 nm $Ge_2Sb_2Te_5$ film. Furthermore, the crystallization slope is much steeper in 30 nm samples.

The crystallization temperatures T_x, as determined in ETTM, are shown in Table I. T_x is defined as the temperature which gives the highest crystallization rate and is determined by the minimum in the first derivative obtained by (dR /dT). T_x increase as the heating rate increases or thickness of GST film decreases. Activation energy for crystallization can be derived by Kissinger plot based on fomula:

$$\ln\left(R/Tx^2\right) = E_{ec}/K_B Tx + X \qquad (1)$$

where, R is the heating rate, Tx is the crystallization temperature at heating rate R, and K_B is the Boltzmann's constant. Figure 2 shows the Kissinger plot for each sample. A good relationship is obtained between $\ln\left(R/Tx^2\right)$ and (R/Tx). The activation energy estimated from the slope of the Kissinger plot are listed in Table II.

In the isothermal measurement (ITTM), samples was kept at temperatures of 143.5 ˚C, resistivity as a function of time was recorded (figure 3). The crystallization processes are analyzed by means of the Avrami coefficient based the Johnson - Mehl - Avrami equation:

$$\chi(t) = 1 - \exp\left[-(kt)^n\right] \qquad (2)$$

where n is the Avrami coefficient and k is an effective rate stant describing both nucleation and growth.

Figure 4 shows the $\ln(-\ln(1-\chi))$ and $\ln t$ plots for each sample. A good linear relationship was obtained in each case. The slopes of these plots shown in figure 4 are corresponded to Avrami coefficients.

3. Discussions

From Table II, it is found activation energy is increased when thickness decreases in nano-crystallization. This increase is due to the higher effective specific interface energy between dielectric and $Ge_2Sb_2Te_5$ in nano- crystallization process[2]. There is no perfect crystalline and oxide interface, therefore, a non-perfect crystalline layer of magnitude of only a few lattice constants would exist near the interface. When the $Ge_2Sb_2Te_5$ film thickness reduced to nano-scale, the activation energy should take non-perfect crystalline layers into account.

The Avrami coefficients is found to decrease from 1.65 at 30 nm to 0.85 at 5 nm. It is well known that Avarami coefficient is an integer providing information on the dimensionality of the crystallization process. Normally, n<1.5 represents one dimensional grain growth from the nuclei; 1.5<=n <2.5 represents nucleation rate decreases with process of the grain growth; and n>=2.5 represents nucleation rate increases with the progress of grain growth. Therefore, it is obvious that above 20 nm, GeSbTe films have crystallization process in which grain growth occurs with nucleation. Its nucleation rate decreases with process of the grain growth. When the film was reduced to nano-scale, the grain only grows in parallel dimension.

4. Effect on Devices

In line-type PCRAM, phase change film is very thin and

their thickness significantly affects the programming current and device performance in this structure.

Based on the nano-crystallization discussed above, higher activation energy would enhance the thermal stability of amorphous state in memory.

In another hand, the one dimension grain growth would reduce the crystallization speed and affect the device performance. However, it might be used for multilevel storage because of its relatively gradual crystallization process.

This result and approach used in this work can also be used to estimate the scaling limit of PCRAM, both for vertical and line-type structure.

5. Conclusions

In this paper, thickness dependent nano-crystallization was systematically investigated. The crystallization mechanism in different thick $Ge_2Sb_2Te_5$ films was discussed based on their activation energy and the Avrami coefficient. Its effect on the line-type PCRAM devices was also analyzed. It was found to be beneficial for device thermal stability and multilevel storage application.

References

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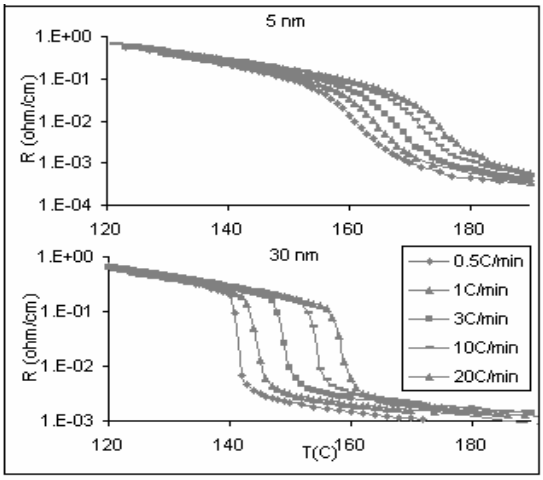

Fig. 1 ETTM of 5 nm and 30 nm $Ge_2Sb_2Te_5$ thin films at different heating rate

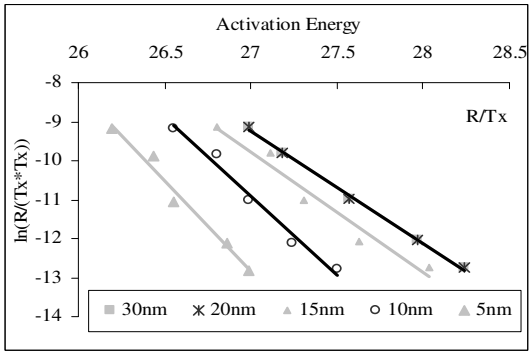

Fig. 2 Kissinger Plot of Ultra-thin GeSbTe films

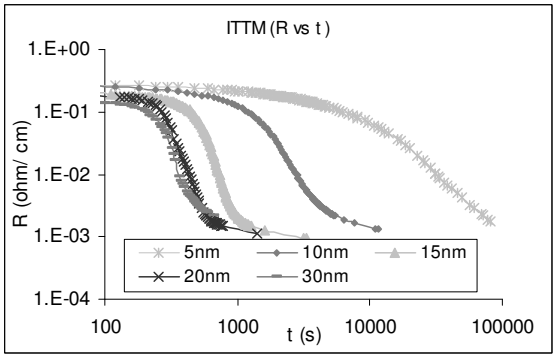

Fig. 3 ITTM of 5 nm, 10nm, 15 nm, 20 nm and 30 nm $Ge_2Sb_2Te_5$thin films at different temperature

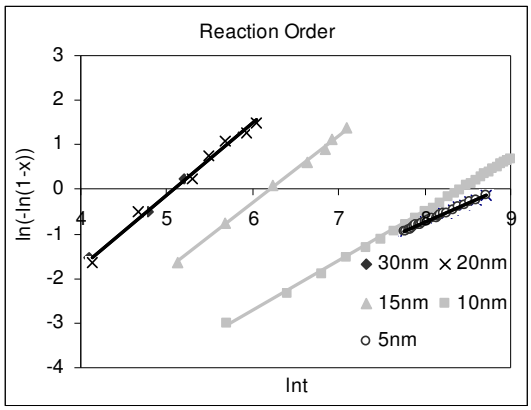

Fig. 4 Avrami Plot of Ultra-thin $Ge_2Sb_2Te_5$films

Table I Crystallization points (˚C) by ETTM

R(˚C/ min)	5nm	10nm	15nm	20nm	30nm
0.5	157	149	141	138	138
1	159	153	147	142	142
3	164	157	152	148	148
10	166	160	155	154	154
20	170	164	160	157	157

Table II Activation Energy (Ea) & Avrami coefficient (n) in Ultra-thin $Ge_2Sb_2Te_5$ films

	5nm	10nm	15nm	20nm	30nm
Ea (eV)	4.66	4.06	3.11	2.86	2.86
n	0.85	1.118	1.501	1.616	1.621