A Study on the Thermal, Electrical Characteristics of Ge-Se-Te Chalcogenide Material for Use in Phase Change Memory

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$Ge_1Se_1Te_2$ chalcogenide amorphous materials was prepared by the conventional melt-quenching method. Samples were processed by e-beam evaporator systems and RF-sputtering systems. Phase change characteristics were analyzed by measuring glassification temperature, crystallization temperature and density of bulk material. The thermal characteristics were measured at the temperature between 300 K and 700 K, and the electrical characteristics were studied within the range from 0 V to 3 V. The obtained results agree with the electrothermal model for Phase-Change Random Access Memory.

Keywords : Chalcogenide, Amorphous, $Ge_1Se_1Te_2$, PRAM

1. INTRODUCTION

Since electrical switching phenomenon using non-crystalline chalcogenide materials was discovered, there is increasing weight on the studies of non-crystalline materials[1,2]. Recently the applications are expended to a variety of industrial fields including thin-film transistor element materials and the next-generation memories using switching phenomenon of chacogenide thin film, secondary battery using the characteristics of optical medium, solar cell, electrolyte, etc. It is because the optical and electrical characteristics that non-crystalline chalcogenide materials have are very excellent[3-6].

As chalcogenide material of bulk state is very easy to be manufactured in thin film, it is possible to be applied to microminiaturized devices and it shows very excellent characteristics in fast switching speed, low power consumption, long life, intimacy with existing processes, etc.. Accordingly, chalcogenide material is being used as core material of phase change memory known well as PRAM of the next-generation memories, and as the studies on it are being actively discussed, in the present study as well, the characteristics were studied after PRAM elements using chalcogenide materials were made.

In the present study, using the non-crystalline chalcogenide material obtained by combining three elements of Ge-Se-Te, thermal characteristics and electrical properties of phase change memory(PRAM) elements were studied. The variation of generated resistance was observed and DC conductivity in the state of high resistance and low resistance was calculated.

2. EXPERIMENTS

After the weight of Ge-Se-Te which had purity of 5 N was measured to 1×10^{-4} g in ratio of atomic weight of 1 : 1 : 2, non-crystalline chalcogenide material was made by melting and cooling method. Sample was made in the structure as Fig. 1. After deposition Al of 1000 Å by lower electrode on Si substrate cleanned in SPM method, SiO_2 700 Å and non-crystalline $Ge_1Se_1Te_2$ 1000 Å were again deposited, and on that, Al upper electrode was deposited.

The manufactured sample had a structure of self-heating method and the contact area between lower electrode and chacogenide material was 12.56 μm^2. The density of $Ge_1Se_1Te_2$ was measured using PENTA PYCNOMETER applied with Archimedes laws and temperature were applied from normal temperature using semiconductor parameter analyzer 4155B, varying resistance and variance of current were observed. Glassification temperature, crystallization temperature and density of bulk material were measured using DSC and Archimedes' theory.

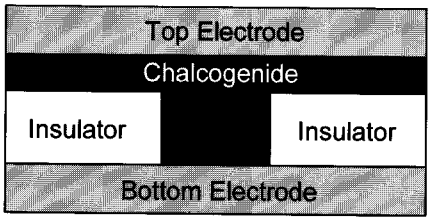

Fig. 1. A cross section of manufactured sample.

3. RESULTS AND DISCUSSION

3.1 Basic parameter of bulk samples

In non-crystalline chalcogenide material which is core material of phase change memory, the combination arrangement of atoms is changed by thermal energy. The phase change by rearrangement of atoms is a very important switching procedure deciding performance of memories in PRAM. In order to form crystalline state or non-crystalline state, there is need to heat over crystallization temperature(Tc) and glassification temperature(Tg), and so it can be said to be a considerably important factor because the intensity of input pulses is affected according to the temperature necessary in each procedure. Especially in changing procedure from crystalline structure to non-crystalline, there is need for relatively higher voltage pulses than the reverse case, so this is a essential part to reduce consumption power that is the biggest issue in PRAM. The result of $Ge_1Se_1Te_2$ thermally analyzed by Differential Scanning Calorimetry(DSC) was shown in Fig. 2.

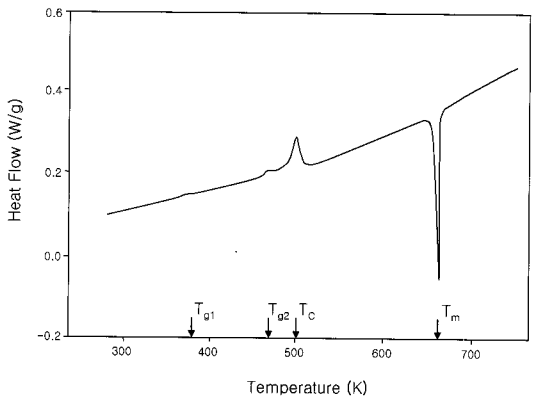

Fig. 2. DSC analysis curve with $Ge_1Se_1Te_2$ bulk material.

From Fig. 2, it can be known that crystallization temperature is about 504.7 K and eutectic temperature is about 669.9 K. Also a tiny peak near 383.2 K is the first phase change temperature and another tiny peak near 476.2 K can be said to mean to be the second phase change temperature.

The density of material is closely connected to other physical characteristics. The density of $Ge_1Se_1Te_2$ was calculated through a procedure that the mass obtained using PENTA PYCNOMETER is divided by volume and was confirmed with a equation through equation 1.

$$V = \frac{xM_a + yM_b + zM_c}{d} \tag{1}$$

At the upper formula, x, y and z are atomic percentage of elements a, b and c, M_a, M_b and M_c are the atomic weight each of elements and d the obtained density of the corresponding composition. The value of density obtained with equation 1 was 4.62 gm/cm^3 and was a little different from the value obtained by measurement, but in the present study, it was written on the basis of measured value.

Table 1. Density, Tg values of amorphous $Ge_1Se_1Te_2$.

	Tg (K)	d (gm/cm^3)
$Ge_1Se_1Te_2$	476.2	4.81
$Ge_1Se_8Te_1$	378	4.52

Table 1 shows glassification temperature(Tg) and desity(d) of $Ge_1Se_1Te_2$ and $Ge_1Se_8Te_1$[7]. The difference of glassification temperature(Tg) of $Ge_1Se_1Te_2$ and $Ge_1Se_8Te_1$ is mostly affected by binding force between individual atoms and shows the characteristic proportional to the density. The relation between Tg for formation of atoms and density can be analyzed referencing binding energy between mutual atoms of Ge, Se, Te shown in Table 2[8].

Table 2. Values of bond energy of Se-Se, Te-Te, Ge-Ge, Ge-Se, Ge-Te and Se-Te.

Molecules	Bond energy (kJ/mol)
Se-Se	189.22
Te-Te	142.35
Ge-Ge	205.57
Ge-Se	231.11
Ge-Te	172.08
Se-Te	187.57

The binding energy between atoms centered on Te can be seen to be smaller than the binding forces of other atoms. Comparing $Ge_1Se_1Te_2$ with $Ge_1Se_8Te_1$, as formation of $Ge_1Se_1Te_2$ contains 50 % of Te, the density decided by binding force between atoms and Tg are expected to have low values, but on the contrary, they were measured in higher values. Relatively more content of Ge atom of $Ge_1Se_1Te_2$ than $Ge_1Se_8Te_1$ may increase the binding of Ge-Ge and Ge-Se and have high binding energy as much as exceeding the reduced portion of the binding energy by the increase of Te atom, and this can be interpreted to be a factor forming higher density and Tg. Tg of $Ge_1Se_1Te_2$ showed relatively high values, but normally is supposed to have lower temperature than crystallization temperature (Tc), and because Tg, lower than 378 K, is the temperature possible to increase sufficiently according to the conditions in nature and there is possibility to induce matters of reliability, Tg of 443.2 K can be interpreted to be appropriate. And also it can be analogized that $Ge_1Se_1Te_2$ whose density is higher has more stable composition.

3.2 The changes of resistance and DC conductivity

The behavior mechanism of phase change memory is closely related to temperature. Joule heat induced by applied voltage becomes energy that enables medium to be changed into non-crystalline and crystalline state. Figure 3 is the graph that measured the variation of resistance according to temperature. The sample manufactured in non-crystalline state of initial high resistance was heated with increasing temperature from room temperature.

The sample that had shown a little reduced resistance according to increasing temperature showed a abrupt drop when it reached 391 K. The resistance of this point was average 5.93×10^6 Ω and 10.187 Ω, and showed resistance ratio of approximately 5.8×10^5 Ω. This larger resistance difference can give enough discrimination between on and off state, so it can be said to be appropriate for memory components.

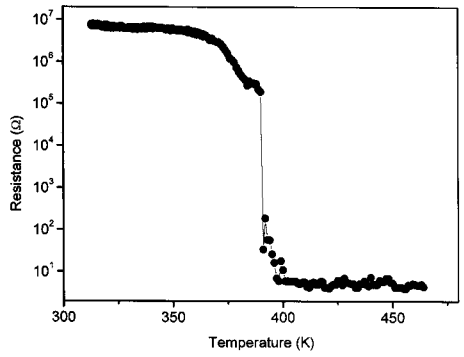

Fig. 3. Resistance change by temperature of $Ge_1Se_1Te_2$ thin film.

As seen in Fig. 3, the resistance by temperature increase in the portion from above 350 K to below 390 K can be observed to drop continuously. A small amount of resistance decrease in non-crystalline section of this high resistance is bound to accompany the change of DC conductivity, which was shown in Fig. 4 after calculating with Equation 2. Figure 4 is the graph of the result of measured DC conductivity according to increasing temperature at temperature below Tc. The obtained results, illustrated in Fig. 4 as lnσ versus temperature(K) satisfy the

$$\sigma = \sigma_0 \exp\left(\frac{-E_\sigma}{k_b T}\right) \quad (2)$$

where σ_0 is the pre-exponential factor, k_B the Boltzmann constant, T the absolute temperature and E_σ the conduction activation energy.

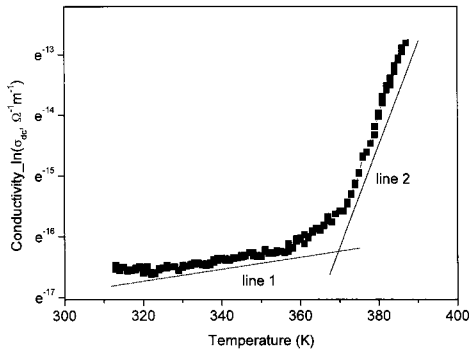

Fig. 4. Temperature dependence of DC-conductivity for $Ge_1Se_1Te_2$ thin film.

The medium of initial phase change of the sample was manufactured in state of non-crystalline state. According to Mott and Davis' theory[9,10], there appear two kinds of electrical conduction, the first is conduction by hoping and the second is conduction by excited carriers at the edge portion of movement way which is not internationalized yet. As seen in Fig. 4, the slope of the graph above and below near 370 K can be seen to have formation of two types. The portion of low slope(line 1) corresponds to conduction by hoping of the contents explained earlier and is a phenomenon occurring at low temperature. On the other hand, the portion of steep slope above 370 K(line 2) is a conduction phenomenon by carriers located at the end portion of movement way and is a form of conduction appearing at high temperature.

The measured values of current change according to increasing temperature are shown in Fig. 5. In the same manner, abrupt current increase by resistance decrease

occurred at 391 K. Because the maximum current value possible to measure by the measuring device is 0.1 A, there is need to be careful of the current of on-state being identical at 0.1 A in Fig. 5. Although there is minute change of current at below 391 K, this is change of current by conduction of non-crystalline state and is considered by two kinds of conduction models discussed earlier. The resistance ratio of non-crystalline state and crystalline state reaching 0.58 MΩ generates excessive change of current as Fig. 5 and can be a ground distinctly deciding on-state and off-state which must be necessarily discrete in memory elements.

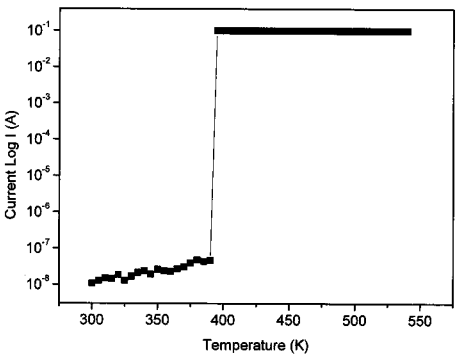

Fig. 5. Temperature dependence of current for $Ge_1Se_1Te_2$ thin film.

4. SUMMARY AND CONCLUSION

In the present paper, in order to apply non-crystalline $Ge_1Se_1Te_2$ material to PRAM, glassification temperature, crystallization temperature and density, DC conductivity and thermal, electrical characteristics that are basic parameters were measured.

Binding energy between atoms affects density of compounds and the mutual binding energy of three atoms of Ge, Se, Te was compared and analyzed.

Measuring the change of electrical characteristics of the sample after applying temperature, the phenomenon of change from high resistance state to low resistance state could be observed at approximately 391 K. It is analogized that phase change into crystalline structure occurred because rearrangement occurred by thermal energy applied in this initial non-crystalline state. At this time, it could be confirmed that the ratio of on-off of resistance by phase change was average over 10^5 times. Also resistance change in non-crystalline state below 391 K could be explained in connection with conduction characteristics in non-crystalline material presented by Mott and Davis.

In this paper, we could confirm the possibility of application of PRAM component using $Ge_1Se_1Te_2$ to memory component by measuring the resistance change by heating of it.

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