JOURNAL OF MATERIALS SCIENCE 26 (1991) 3271–3274

Some properties of $Sb_2Te_{3-x}Se_x$ for nonvolatile memory based on phase transition

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Composition dependence of properties of $Sb_2Te_{3-x}Se_x$ in the range $0 \leqslant x < 3$ were studied using differential thermal analysis and X-ray diffraction. $Sb_2Te_{3-x}Se_x$ form solid solution for $0 < x \leqslant 1.25$ and $2.75 \leqslant x < 3$. A systematic study of crystallization temperature in $Sb_2Te_{3-x}Se_x$ $(0 \leqslant x \leqslant 2.75)$ thin films prepared by flash evaporation was carried out. In preliminary experiments for some compositions, more than 10^3 repetitions between amorphous and crystalline states were attained by the application of electric pulses.

1. Introduction

The chalcogenide amorphous semiconductors have attracted much attention because of their interesting electrical, optical and thermal properties including threshold and memory switching [1–3]. Threshold switches are made in those glasses near the centre of the glass-forming region where the glasses are stable and show little or no tendency to crystallize when heated or cooled slowly. Memory switches come from the boundaries of the glass-forming region where the glasses are more prone to crystallization [4].

Recently, it is shown that the amorphous films with composition outside the glass-forming region are more suitable for memory devices because of their fast crystallization during the application of a suitable electric pulse or by the heat of a focused laser beam. In fact it has been shown that Ge_xTe_{1-x} $(x \leqslant 0.1)$ and Sb_xTe_{1-x} $(x \leqslant 0.2)$ films can be cycled between the amorphous and the crystalline state for more than 10^4 cycles using electric pulses [5]. Tellurium alloys have often been used for the active layer of those devices because they have low melting point.

Those Te-based alloys which contain a small amount of Ge, As or Sb exhibit fast crystallization processes after switching. However, these alloys present several problems, for example, segregation and low crystallization temperature. In fact, Ge_xTe_{1-x} $(x < 0.1)$ and Sb_xTe_{1-x} $(x < 0.2)$ have crystallization temperature lower than 100 °C, hence the data retention in the amorphous phase is limited. The segregation limits the reversible transition between crystalline and amorphous states, because in every crystallization process the compositional deviation is likely to continue in the active layer. A ternary solid solution with relatively low melting point may be the answer to the above problems, because no compositional changes occur in a solid solution when it is cycled between amorphous and crystalline states.

In this paper we report our studies on $Sb_2Te_{3-x}Se_x$ ternary solid solution. The melting point, crystallization temperature and electrical conductivity measurement are given. Preliminary studies on memory devices fabricated from these ternary compounds are presented.

2. Experimental details

For preparing the polycrystalline $Sb_2Te_{3-x}Se_x$ $(0 \leqslant x < 3)$ bulks, proper quantities of high-purity elements (99.999%) were sealed in an evacuated quartz ampoule and heated in a rocking furnace up to 700 °C for more than 24 h. The melts were slowly cooled by switching off the furnace to obtain polycrystalline materials. The melting point of the prepared polycrystalline samples was measured using a Rigaku thermal analyser with a uniform heating rate of 10 °C min^{-1}. The samples were always heated in a nitrogen atmosphere for differential thermal analysis (DTA) work to avoid oxidation. A Rigaku X-ray diffractometer was used to identify the phases present in the polycrystalline material. The diffraction studies were carried out using CuK_α X-rays with $\lambda = 0.154\,18$ nm. An intensity–2θ plot was made using a powder sample spread on cellophane tape.

The electrical conductivity and crystallization temperature were measured for flash-evaporated films with coplaner electrode configuration. The measuring cell was evacuated to $\sim 1 \times 10^{-2}$ torr (1 torr = 1.333×10^2 Pa) during the electrical conductivity measurement. The crystallization temperature was determined by the transition (in conductivity) in the Arrhenius plot of conductivity. The heating rate was 2 °C min^{-1}.

The structure of the memory cells used for studying the phase transition by the application of electrical pulses was a sandwich structure in which chalcogenide semiconductor films were inserted between two electrodes. Other experimental details have been reported in our earlier publication [5].

3. Results and discussion

In DTA measurements of the $Sb_2Te_{3-x}Se_x$ system with $0 < x \leqslant 1.25$, one sharp endothermic peak was seen, while another diffused peak at higher temperature appeared in materials with $x \geqslant 1.5$ and became intense with increasing x. The sharp peak became smaller with increasing x and disappeared at $x = 2.75$. The materials are, thus, single phase in the region with $x \leqslant 1.25$ and $x \geqslant 2.75$, but those with $1.5 \leqslant x \leqslant 2.5$ are a mixture of two phases.

The melting points of the $Sb_2Te_{3-x}Se_x$ system obtained by DTA are shown in Fig. 1. The lower melting point, T_{m1}, remains almost unchanged with selenium content, x, up to 2.5 after a sharp decrease from 621 °C of Sb_2Te_3. On the other hand, the higher melting point, T_{m2}, gradually decreases from 618 °C of Sb_2Se_3 and then slightly increase with tellurium content. It is noted that T_m of Sb_2Te_3 decreased from 621.6–410 °C by the substitution of only 8 at % of Te with Se.

X-ray diffraction patterns of $Sb_2Te_{3-x}Se_x$ for small x were similar to those of Sb_2Te_3, which has hexagonal structure [6]. The diffraction lines of this pattern shifted towards higher angle with increasing x and the intensity decreased rapidly above $x = 2.0$. This diffraction pattern is assigned to the hexagonal structure in which the lattice parameters are shrunk by the substitution of Te by Se into the hexagonal Sb_2Te_3.

Another diffraction pattern appeared in the materials with $x > 2.25$ and increased with x. This pattern is assigned to orthorhombic structure which is distorted by the substitution of Se by Te into orthorhombic Sb_2Se_3 [6]. The shift of the diffraction angle in this pattern occurred mostly between $x = 2.75$ and 3, that is, between $Sb_2Se_{2.75}Te_{0.25}$ and Sb_2Se_3.

The variation of lattice constants for the hexagonal and orthorhombic phase was calculated from X-ray diffraction patterns and the results are shown in Fig. 2. Both a and c values are shown for the hexagonal structure, but for the orthorhombic structure only c values are shown. Although the results of DTA suggest that there are both hexagonal and orthorhombic phases present in the region with $1.5 \leqslant x \leqslant 2.5$, the diffraction lines from orthorhombic structures could not be detected in those materials with $1.5 \leqslant x \leqslant 2.5$, because of the rapid decrease of the intensity of the diffraction lines from the orthorhombic structure below $x = 2.5$. The same situation occurred for the hexagonal structure above $x = 2.25$.

The lattice parameters showed a continuous decrease with increasing x in the case of hexagonal structures. It is reasonable that the incorporation of Se into the hexagonal Sb_2Te_3 makes the lattice parameters small [7], because the radius of the Se ion is smaller than that of Te. On the other hand, the incorporation of Te into the orthorhombic Sb_2Se_3 is expected to expand the lattice constants of the orthorhombic phase. This situation is seen for the compositions with $x \geqslant 2.5$ in Fig. 2, but the expansion of the lattice constants of orthorhombic structures appears to be saturated by the substitution of Se at about 15 at % Te.

In the compositions with $1.5 \leqslant x \leqslant 2.5$, there are both hexagonal and orthorhombic crystals, so that for a certain value of x two structures share Te and Se, such as $Sb_2Te_{3-(x-\delta)}Se_{x+\delta}$ for hexagonal and $Sb_2Te_{3-(x+\delta)}Se_{x-\delta}$ for orthorhombic, where δ is smaller than unity. Taking these situations into account, the maximum substitution of Se by Te in the orthorhombic Sb_2Se_3 is estimated to be less than

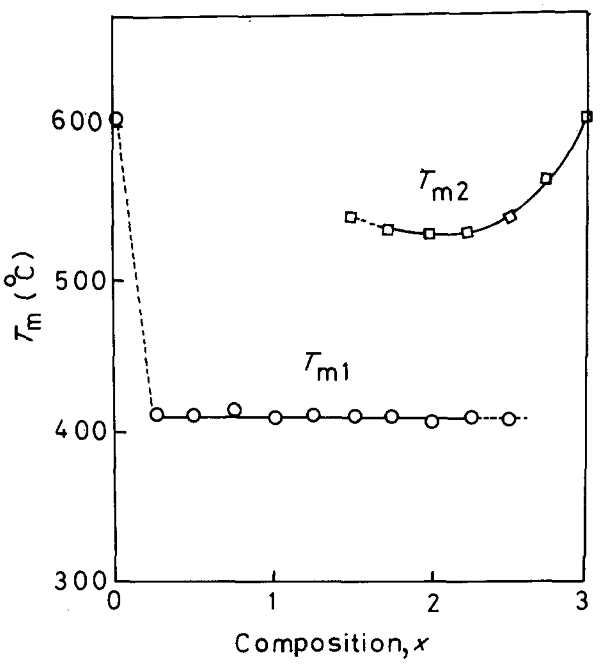

Figure 1 Composition dependence of melting point, T_m, in polycrystalline $Sb_2Te_{3-x}Se_x$. T_{m1} and T_{m2} are the melting points for hexagonal and orthorhombic crystals, respectively.

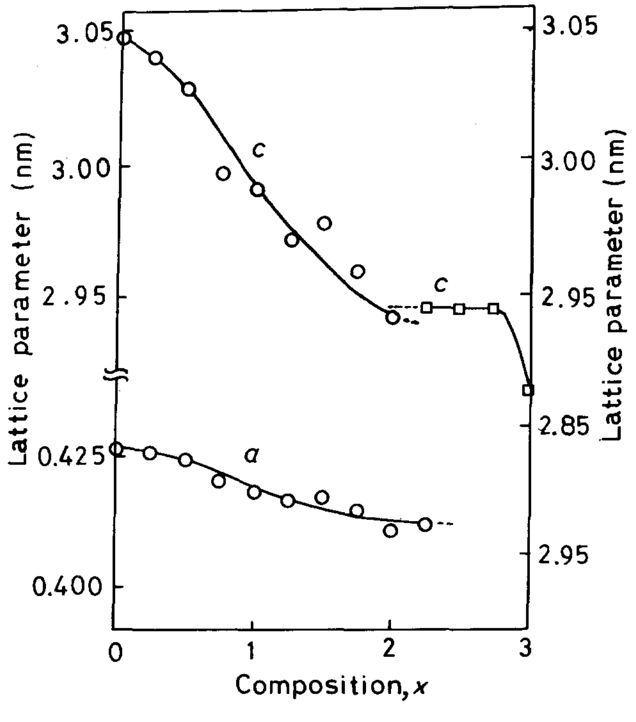

Figure 2 The variation of lattice constants as a function of x in $Sb_2Te_{3-x}Se_x$, calculated from X-ray diffraction patterns. (○) Hexagonal, (□) orthorhombic.

10 at %. That is the orthorhombic structure with the maximum Te concentration would be expressed by $Sb_2Te_{\sim 0.3}Se_{\sim 2.7}$. On the other hand, hexagonal structures starting from Sb_2Te_3 appear to be retained even for Sb_2TeSe_2. It is very interesting to note that the hexagonal structure starting from Sb_2Te_3 is preserved even after more than 3% lattice distortion; on the other hand, the orthorhombic structure of Sb_2Se_3 cannot bear even 1% lattice distortion due to the substitution of Se by Te.

In memory devices using different electrical and optical properties in the crystalline and amorphous states, a lower melting point is preferable, because the crystalline state can be converted to the amorphous state by laser beam or electric pulse with relatively lower energy. Moreover, those solids forming a solid solution are preferable, because phase separation or segregation do not occur in the transition from the amorphous to the crystalline state. Phase separation or segregation in crystallization processes is one cause of degradation of memory devices. From these points of view, $Sb_2Te_{3-x}Se_x$ with $x \leqslant 1.25$ are suitable materials for memory devices.

A higher crystallization temperature is also necessary for memory devices. The crystallization temperature, T_c, was measured using amorphous $Sb_2Te_{3-x}Se_x$ films which were prepared by flash-evaporation. Although the composition of films measured by electron probe microanalysis (EPMA) is slightly different from the evaporation source, the same formula as that of the bulk is used here for evaporated films.

T_cs determined from the variation of the conductivity with temperature are shown in Fig. 3. T_c of the evaporated films of $Sb_2Te_{3-x}Se_x$ increases monotonically with increasing x and films with $x \geqslant 0.5$ exhibited T_c higher than 100 °C. T_c is known to be related to the molecularity and the band gap of glasses. The substitution of Te by Se widens the band gap, and is expected to somewhat change the molecularity of the glasses [8], so it is reasonable for T_c to increase with increasing Se content.

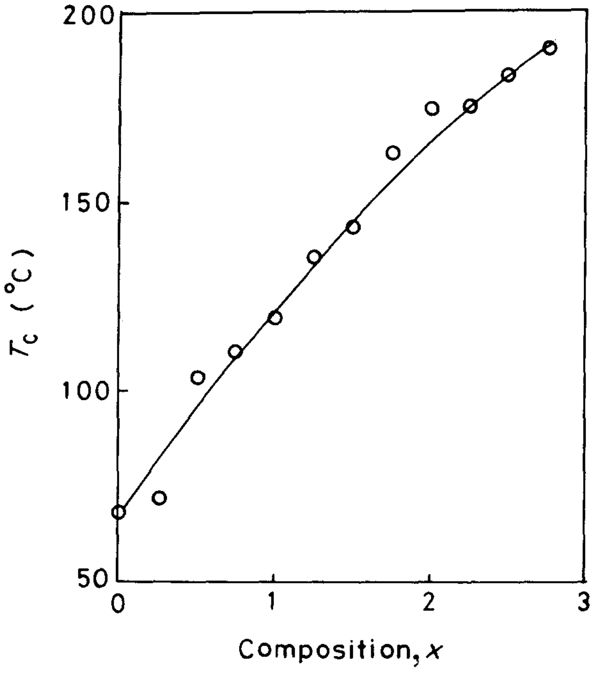

Figure 3 Composition dependence of crystallization temperature, T_c, in flash-evaporated $Sb_2Te_{3-x}Se_x$ thin films.

From the thermodynamical point of view, the compositional region suitable for memory devices is thus limited to $0.5 \leqslant x \leqslant 1.25$. In a preliminary experiment on memory devices using evaporated films of $Sb_2Te_{2.5}Se_{0.5}$, more than 10^3 repetitions of the phase transition were attained. The mode of degradation is a gradual lowering of the resistivity in the amorphous states with the repetitions. This is due to the segregation or phase separation which cannot be avoided in crystallization processes in materials with compositions differing from the stoichiometric $Sb_2Te_{3-x}Se_x$ $(0 < x \leqslant 1.25)$. The composition deviation of the evaporated films from the evaporant is known to occur in binary or ternary alloys during evaporation [9]. If thin films with stoichiometric composition are prepared, many more repetition cycles of the phase transition are expected to be attained.

4. Conclusions

$Sb_2Te_{3-x}Se_x$ alloys form a solid solution in the regions with $0 < x \leqslant 1.25$ and $2.75 \leqslant x < 3.0$. Both hexagonal and orthorhombic crystals form in the region with $1.25 < x < 2.75$, e.g. $Sb_2Te_{3-(x-\delta)}Se_{x+\delta}$ for hexagonal and $Sb_2Te_{3-(x+\delta)}Se_{x-\delta}$ for orthorhombic, where δ is smaller than unity. It is noted that less than 10 at % Se can be substituted by Te in the orthorhombic structure of Sb_2Se_3, while the hexagonal structure of Sb_2Te_3 is retained even for Sb_2TeSe_2.

The samples with $0.5 \leqslant x \leqslant 1.25$ are expected to be suitable for memory devices using the difference in reflectivity or electrical conductivity between the crystalline and amorphous states, because they possess a T_c higher than 100 °C, have a fairly low melting point and they are in single phase in the crystalline states.

The preliminary results on memory devices are very promising. More than 10^3 repetitions of the amorphous to crystalline state and vice versa were attained for the composition $Sb_2Te_{2.5}Se_{0.5}$.

Acknowledgements

The authors thank Dr K. Torii, Mr Kakimoto and Mr Ishimoto for their help with the experiments. One of the authors (DPG) gratefully acknowledges the grant of a scholarship from the Ministry of Education, Science and Culture, Government of Japan.

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Received 19 April
and accepted 6 November 1990