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Phase change materials: chemical bonding and structural properties

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Abstract

Phase change materials are the most important materials in the class of chalcogenides (combination of chalcogens (S, Se, Te) with metalloids and metals).
The outstanding property of these materials is the switching from a high electrical resistivity state to low electrical resistivity state and back under a moderate voltage. The thin film materials are used in computer memories, CD and DVD devices with performing speed and storage capacity.
We have studied several thin solid films made of Ge – Sb – Te in order to assess the switching quality of different compositions.
In order to systemize the whole class of chalcogenide phase change materials we have investigated the correlation between different crystallo-chemical parameters and the ionicity of the elements.
Binary and ternary compounds are distributed into several distinct groups. The most favorable phase change materials, are situated in a specific range of mean ionicity and mean glass formation ability. The results give possibility to design new compositions with better switching properties.

Introduction

Switching effect in amorphous materials has been discovered by Ovshinsky in 1968 [1]. The effect consists in changing the resistance of a thin film under the influence of a short electrical pulse applied to the material. Figure 1 illustrates the effect. The electrical switching is characterized by the treshold voltage, threshold current, resistivity change from amorphous to crystalline phase and the rapidity of the phase transition (amourphous to crystalline and back).

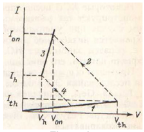

Figure 1

Crystallo-chemical parameters

In order to relate the switching parameters on the crystallo-chemical characteristics of a chalcogenide material we introduced two parameters: the reduced ionicity (RI) and the Glass ability (GA). $RI = \frac{I_i}{\eta}$ is the mean ionicity of the compound divided by η, the weighted mean of the inverse of the orbital radius in the compound or alloy. Glass ability is defined by $GA = \frac{\bar{n}\bar{k}}{\bar{Z}}$ where $\bar{n}$ is the mean value of the last orbital occupied by electrons, $\bar{k}$ is the mean coordination number and $\bar{Z}$ is the mean of the atomic number of atoms entering into the composition of the material.
As switching parameters were taken into account: the threshold potential (V_{th}) for switching, the resistivity of the material and the number of cycles supported by a given material.

Results

Ge – Sb – Te system

One of the most important chalcogenide system used in switching is Ge – Sb – Te. Tellurium seems to be an essential element that ensures the rapidity, reversibility and stability of the switching along many cycles. The ternary phase diagram is shown in Figure 2. The switching compositions, well studied, are represented by black dots.

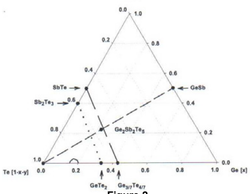

Figure 2

We have transformed the usual phase diagram in a special one related to crystallo-chemical parameter RI. (Figure 3). During switching the structural properties of the material changes from the crystalline state to the amorphous state. In this system the most important modification is the change in coordination from octahedral one (as demonstrated in $GeSb_2Te_4$ to the natural coordination of every type of atom (4 for Ge, 3 for Sb and 3 for Te). As a consequence the points from the crystallo-chemical triangle shift to various positions as a function of the quality of switching. A careful analysis of the switching is necessary in order to get the structural data.

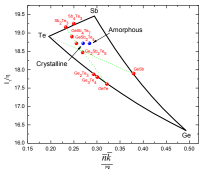

Figure 3

Ge – As – Te – Se system

Similar correlations are found in the system Ge – As – Te with Selenium. All the graphs speak in favour of a strong dependence of the switching quality on the ionicity of the material.

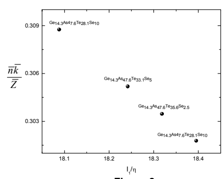

Figure 8

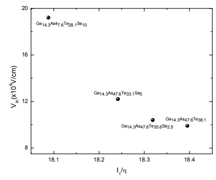

Figure 9

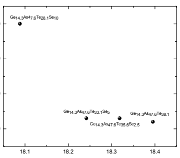

Figure 10

As – Se – Te system

We have analyzed the switching in the system As_2Se_3-As_2Te_3 as a function of the parameters: GA and RI. Figs. 4 - 6 show the results. The correlation between the two parameters GA and RI is linear. The correlation of the ionicity with threshold voltage and resistivity is also evidenced. The threshold voltage decreases with the ionicity of the material. The resistivity decreases, too, with ionicity.

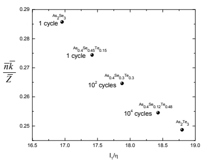

Figure 4

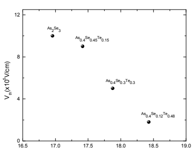

Figure 5

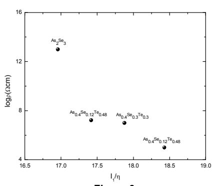

Figure 6

Ge – Si – As – Te system

The quaternary system behaves similarly. Essentially the resistivity increases with the mean ionicity of the material.

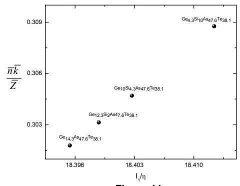

Figure 11

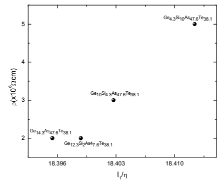

Figure 12

Differences in resistivity

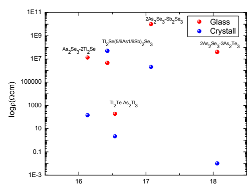

Figure 13

Conclusions

The properties of the switching chalcogenide materials depends strongly on the chemical characteristic of the material. The ionicity is the most important factor. The glass ability is also important. Materials which easily form glasses exhibit better switching properties. The difference of the resistivity in the crystalline and amourphous state seems to depend of the ionicity of the material (Figure 13).

Acknowledgement

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References

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