GLASSY TRANSFORMATION AND STRUCTURAL CHANGE IN $Ge_2Sb_2Te_5$ STUDIED BY IMPEDANCE MEASUREMENTS

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The transition form amorphous-to-crystalline (fcc) has been investigated in $Ge_2Sb_2Te_5$ thin film alloys. This composition is the most frequently used for erasable optical memory devices. The phase transition was monitored using *in situ* impedance measurements as a function of temperature. The results were analyzed using the Maxwell-Wagner and brick models. From the impedance measurements it is possible to detect the appearance of nucleation centers in samples heated at temperatures below crystallization. In samples treated at temperatures above crystallization, the increase in the volume fraction of crystalline material due to the increase in the temperature is also deduced from the impedance measurements. From our investigation we have shown that impedance measurements are a sensitive method to analyze the crystallization process in chalcogenide materials.

1. Introduction

Glassy chalcogenide semiconductors have been studied extensively due to their applications in optoelectronics and electronics. Some of these applications are based on the difference in the optical and/or electrical properties between the amorphous and crystalline phase. The Ge:Sb:Te ternary alloys are the active materials most frequently used in phase-change optical memory technology, specifically, due to its fast crystallization the $Ge_2Sb_2Te_5$ composition has been used in commercial optical devices. Upon annealing, amorphous layers of this material first undergo the amorphous-to–crystalline (fcc) transition at about 165 ^{o}C and at higher temperatures (at about 230 ^{o}C) the crystal (fcc)-to-crystal (hex) transition. The crystallization mechanism in these alloys has been studied by many techniques such as optical [1-3], electrical [4-6], Raman spectroscopy [7,8], coherent phonon spectroscopy [9], X-ray diffraction [7,10], transmission and scanning electron and atomic force microscopy [2, 5, 11, 12]. In general, the aim of these investigations is to determine the activation energy of the phase transformation, the microstructures changes in the material during thermal and laser annealing and the influence of the protecting layers on the crystallization process. However, to our knowledge there is no model that can fully explain the crystallization mechanism in this material.

The aim of this article is to study the crystallization process in amorphous $Ge_2Sb_2Te_5$ ternary thin film alloys by *in situ* impedance measurements as a function of temperature. This technique is vary sensitive to monitor the phase transition, because: i) the resistance of the amorphous state is several orders of magnitude higher than that of the crystalline state [4,5,6], therefore in the process of crystallization a similar change in the real part of impedance must occur; ii) as it is well established in the literature in some temperature range during the process of crystallization, the amorphous and crystalline phase coexisting and the impedance measurements have been widely used for the investigation of the properties of a two-phase materials [13] and   iii) the impedance measurements allow to establish the correlation between the microstructure and electrical properties of the material and to obtain information, such as parameter of grain boundaries, difficult to obtain using other methods.

2. Experimental

The $Ge_2Sb_2Te_5$ thin films were prepared by RF sputtering of the bulk alloy samples onto unheated glass substrate. Film with a thickness ranging from 30 nm to 4.6 micrometers were investigate. The samples were heated using a 300 W resistance cartridge heater. The temperature was controlled with a Watlow´s Series 982, 1/8 DIN microprocessor-based, with ramping controller. The temperature controller was programmed to produce a constant heating rate of 4 $^{o}C/min$ and to stops every 5 degree to make the impedance measurements in the frequency range of 40 Hz-110 MHz. The measurement were done with the help of an Agilent Precision Impedance Analyzer model 4294A. The amplitude of the measurement signal was 500 mV. For the impedance studies the planar configuration was used with evaporated Al or silver paint contacts (distance between contact was varied in the range of 0.7-2 mm). The impedance measurements were carried out in films annealed to temperatures below the fcc-to-hexagonal phase transition. The conductivity of the hexagonal phase is too high for the frequency capacity of our device. The experimental results were fitted using the ZView program to obtain the absolute values of all components of the proposed equivalent electrical circuit.

3. Experimental results

The impedance spectra measured in the samples analyzed in this work depend on the temperature at which the sample is measured. Plots of the imaginary versus real part of the impedance consist of one semicircle (not shown) when the sample is measured at temperatures below approximately 100 ^{o}C and of two semicircles in samples measured at higher temperatures (see Fig. 1). In the former case, the material is amorphous and the semicircle is related with the properties of the material. In some cases, amorphous materials show impedance spectra with two semicircles, in which the low frequency semicircle describes the properties of the electrical contacts [14]. >From the semicircle observed in the impedance spectra of samples measured at temperatures below 100 ^{o}C a value for the dielectric constant in the range of 12.8-15.6 was calculated. The dielectric constant in similar amorphous materials have been reported before, a theoretical steady-state value of 17.7 [15] and also a reported value of 15.3 determined using IR absorption measurements are in good agreement with the experimentally determined in the present work. This confirms the assignment given to the observed semicircle. The resistivity obtained from collinear four-probe measurements (at the room temperature) differs at the most 30 % from the obtained from the impedance measurements in the same material.
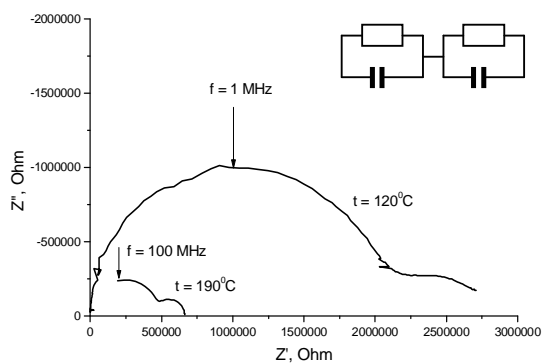

Fig. 1. Impedance spectra obtained at temperatures of 120 ^{o}C and 190 ^{o}C. The real and imaginary part of the spectra obtained at 190 ^{o}C has increased 100 times.
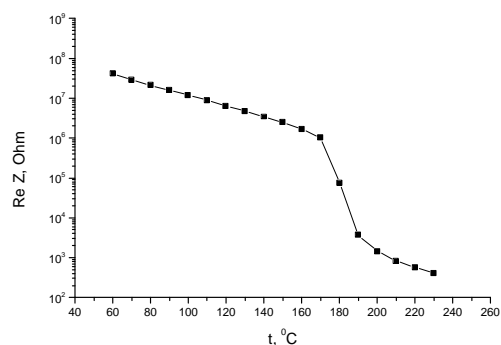
Fig. 2. The temperature dependence of the real part of the impedance.

Arrows show the frequency corresponding to indicate point.

For samples measured at temperatures above 100 ^{o}C but below the crystallization temperature T_c, which is 160-175 ^{o}C for the material studied, the high frequency semicircle is attributed to the resistance and capacitance of the amorphous material (spectrum at 120 ^{o}C in Fig. 1). We suggested that the second semicircle could be due to the appearance of the nucleation centers which start the

crystallization of the amorphous material. This assumption is based on our Temperature-Modulated Differential Scanning Calorimetry measurements in similar Ge$_2$Sb$_2$Te$_5$ samples which indicate that the glass transition temperature T$_g$ for this material is at about 100 ^{o}C. As has been established in the literature, for many chalcogenide amorphous alloys the nucleation appears at temperatures after T$_g$ [16,17]. At temperatures above T$_c$ one can see (spectrum at 190 ^{o}C in Fig. 1) that the impedance spectra also consist of two semicircles, but both semicircles move to higher frequencies. In these spectra, the value of capacitance estimate from the high frequency semicircle is two–three times higher than the value of the capacitance measured for the amorphous material. This is in good agreement with previous results [15] which report that the static dielectric constant of the metastable cubic crystalline phase is 2.2 times larger than that of the amorphous phase. The value of the capacitance determined from low frequency semicircle is about two orders of magnitude larger than the corresponding to the high frequency semicircle, so we suggested that the low frequency semicircle is related with the properties of the grain boundaries. The later is based in two facts: i) our transmission electron microscopy (TEM) measurements in samples heated to temperatures in this range show that the films have a polycrystalline structure [5], and ii) in general the grain boundaries have a higher capacitance than the grain interiors [13]. Fig. 2 shows the temperature dependence of the real part of the impedance spectra, i. e., the resistance of the material as a function of measuring temperature. Qualitative this result is similar to the obtained previously under d.c. [4] or a.c. measurements [5], that is why we do not discuss this dependence.

From the above analysis we can conclude that the structure of samples heated in the range between T$_g$ and temperatures below the crystal-to-crystal transition are formed by a mixture of two phases: at lower temperatures the mixture consists of amorphous and crystalline nuclei, and at higher temperatures the mixture is grains with the fcc structure and grains boundaries. The electrical properties of materials with a structure composed of two phases can be described by an equivalent circuit consisting of two in series RC circuit (this circuit is shown as insert in the Fig. 1).
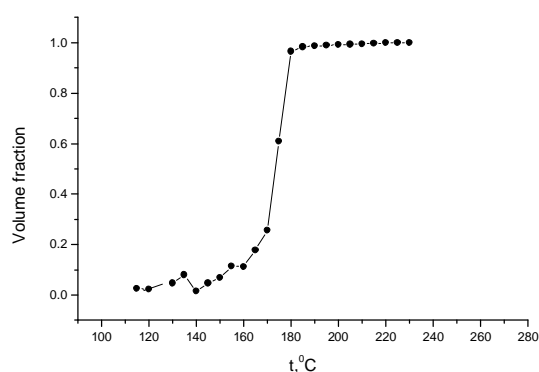

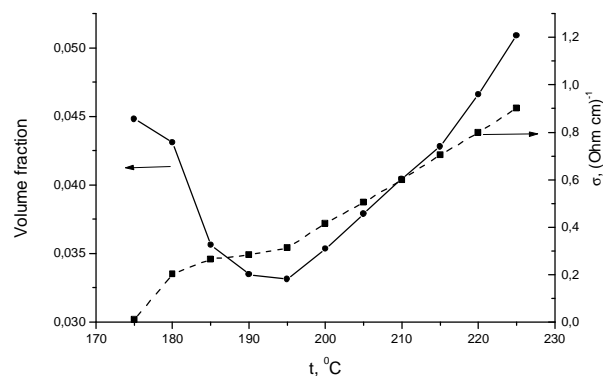Fig. 3. The temperature dependence of crystalline volume fraction.

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Fig. 4. The temperature dependencies of grain boundaries volume fraction (solid line) and conductivity (dot line).

The electrical properties of continuous medium containing uniformly distributed spheres of a different phase are well described by Maxwell–Wagner model. It was shown [18] that this model is equivalent to the two in series RC circuit shown in Fig. 1. Using the Maxwell–Wagner model we can calculate the change in the crystalline volume fraction for temperatures above 100^{0} C. This dependence is shown in Fig. 3. For samples heated at temperature above the amorphous–to-crystalline transition, we can use the brick model [13], which assumes that cubic-shaped grains are separated by flat grain boundaries. Such physical model agrees with the TEM micrographs which show that the material consists of randomly oriented crystallites [5]. Using this model the volume fraction and conductivity of grain boundaries were calculated and are shown in Fig. 4. The relatively high conductivity of the grain boundaries may be explained assuming the appearance of about 20 % of vacancies at the grain boundaries [10].

4. Discussion

Our results have shown that in Ge$_2$Sb$_2$Te$_5$ thin films, the amorphous-to-crystalline transformation occurs after heating at temperatures higher than T$_g$. In the temperature range between T$_g$ and T$_c$ the

nucleation centers appear and increase as the heating temperature approaches T_c. At the initial stages of nucleation, X-ray diffraction measurements did not detect any crystalline peaks, diffraction peaks corresponding to the fcc phase appear when the volume occupied by the crystalline material is of few percentage, this suggest that the nucleation centers have the cubic phase. The impedance spectra of samples treated above T_c consist of two semicircles (Fig. 1). Similar spectra are found when the sample is cooled down to room temperature. The resistance of samples heated above T_c was measured at room temperature using the four-probe method and the results are close to those determined from the room temperature impedance spectra. This implies that these semicircles describe the microstructure properties of the material. According to previous consideration we concluded that low frequency semicircle describes the electrical properties of the grain boundaries. However, applying the brick model to our experimental resells, we have obtained unexpected results: in Fig. 4, the volume fraction of grain boundaries first decreases and than increases with the increase in temperature. In previous studies in similar samples annealed above crystallization it was reported that TEM observation show that the grain size increases with the increase in temperature [2,5]. In principle, this implies that the volume fraction of grain boundaries must decrease. An explanation to the increase in the volume fraction of grain boundaries could be the following. In the reference [10] have shown that the X-ray diffraction data of crystallized $Ge_2Sb_2Te_5$ films contain two phases: one is the $Ge_2Sb_2Te_5$ crystalline phase and another minority phase of elemental Sb which remain in the amorphous phase at the grain boundary. According to this results [10] we proposed that above certain annealing temperature (about 200 ^{o}C), the increase of some atomic segregation to the grain boundaries such as Sb or other impurities could be responsible for the increase in the volume fraction of grain boundaries.

5. Conclusion

It has been shown that the impedance measurements are a high sensitive method by means of which it is possible to determine the structural change in the process of an amorphous-to-crystalline transition. In addition, the impedance study allows to detect the presence of nucleation centers in the early stages of crystallization and to characterize the structural parameters after crystallization.

Reference

[1] A. Mendoza-Galván, J. González-Hernández, J. Appl. Phys. **87**, 1, (2000).
[2] N. Oshima, J. Appl. Phys. **83**, 5244 (1998).
[3] C. A. Volker, M. Wutting, J. Appl. Phys. **86**, 1808 (1999).
[4] I. Friedrich, V. Weidenhof, W. Njoroge, P. Franz, M. Wutting, J. Appl. Phys. **87**, 4130 (2000).
[5] J. González-Hernández, E. Prokhorov, Yu.Vorobiev, J. Vac. Sci. Technol. A, **18**, 1694 (2000).
[6] J. González-Hernández, V. Castaño, A.del Real, E. Morales-Sánchez, E. Garsía-Garsía, A. Mendoza-Galván, E.Prokhorov, Yu.Vorobiev, Inorganic Mat. **36**, 1219 (2000).
[7] J. González-Hernández, B. S. Chao, D. Strand, S. R. Ovshinsky, D. Pawik, P. Gasiorowski, Appl. Phys. Com. **11**, 557 (1992).
[8] J. Tominaga, N. Atoda. Jpn. J. Appl. Phys. **38**, L322 (1999).
[9] M. Forst, T. Dekorsy, C. Tappe, M. Laurenzis, H. Kurz, Appl. Phys. Lett. **77**, 1964 (2000).
[10] N. Yamada, T. Matsunaga, J Appl. Phys. **88**, 7020 (2000).
[11] N. Nobukuni, M. Takashima, T. Ohno, M. Horie, J Appl. Phys. **78**, 6980 (1995).
[12] V. Weindenhof, I. Fiedrich, S. Ziegler, M. Wutting, J Appl. Phys. **86**, 5879 (1999).
[13] J. R. Macdonald. Impedance spectroscopy, John Wiley & Sons. Inc. (1977).
[14] E. Morales-Sánchez, J. González-Hernández, E. Prokhorov, Yu. Vorobiev, M. Becerril, Abstract of Int. Mat. Research Congress, Cancun 2000, p. 16.
[15] R. Yokota. Jpn. J. Appl. Phys. **28**, 1407 (1989).
[16] A. Elshafie, A. Abdel-All. Physica B, **269**, 69 (1999).
[17] Y. Calventus, S. Suriñach, M. D. Baró, J. Mat. Res. **12**, 1069 (1996).
[18] N. Bonanost, E. Lilley, J. Phys. Chem. Solids **32**, 943 (1981).