JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 13, No. 11-12 , November – December 2011, p. 1498 - 1501

Electrical and optical characterization of tellurium free phase-change material

SALEH T. MAHMOUD*, N. QAMHIEH, A. I. AYESH, H. GHAMLOUCHE[a], M. EL-SHAER
U.A.E. University, Department of Physics,Al-Ain, P.O. Box: 17555, U.A.E.
[a]*Department of Physics, American University of Beirut, P.O.Box 11-0236, Beirut, Lebanon*

In this work we investigate the electrical and optical properties of $Ge_{15}Sb_{85}$ thin films –prepared by a DC sputtering technique. The phase transition of Te-free films was studied using resistance–temperature measurements. The structure and stoichiometery of the films were identified by X-Ray Diffraction (XRD), and Energy Dispersive X-ray analysis (EDX). The electrical properties of $Ge_{15}Sb_{85}$ films have been investigated using AC conductivity (Impedance spectroscopy). The resistance-temperature measurements reveal that the amorphous-crystalline transition temperature of $Ge_{15}Sb_{85}$ is around T_C = 420 K. The optical energy gap of $Ge_{15}Sb_{85}$ films has been measured using UV-VIS-IR spectrophotometer. The estimated activation energy and optical gap allocate the Fermi energy level in high density valence band tail states.

(Received June 2, 2011; accepted November 23, 2011)

Keywords: Chalcogenides, Phase change materials, Impedance spectroscopy, Nonvolatile Memories

1. Introduction

The idea of using an amorphous-to-crystalline phase transition for data storage was established in the 1960s when S. R. Ovshinsky suggested a memory switch based upon changes in the properties from amorphous to crystalline phase of multicomponent chalcogenides [1]. Chalcogenides based phase-change materials have been extensively used in optical rewritable data storage media because of the discrete changes in their optical properties that occur due to the phase-transition. The change in optical properties upon phase transition cause a high contrast between amorphous and crystalline regions which enables a straight forward reading of the information [2, 3].

In addition to their high optical contrast, such materials exhibit resistance disparity of several orders of magnitude making them good candidate for the next generation of nonvolatile memory [4, 5]. Phase-change random access memory (PCRAM) is one of the most promising candidates for next generation non-volatile solid-state memory due to its nonvolatility, high speed, low power and low cost [6, 7]. In the past few years, Ge-Sb-Te has been widely used in PCRAM research and development due to its outstanding properties of thermal stability and electrical performance [8-10]. However, its performance was not always satisfactory since Tellurium (Te) has a low melting temperature and high vapor pressure, which may lead to phase separation and reduction of reliability of the material [11].

Novel phase change materials without Tellurium may have a good prospect in the applications of PCRAM. It has been reported recently that Ge-Sb with low percentage of Ge shows a promising switching behavior [12 - 15]. It showed a higher crystallization temperature than a Te based phase change material which is promising in terms of data retention. The need for further improvements in speed, data retention, and switching voltage is driving an intensive search for new and optimized phase change materials. In this work, Te-free $Ge_{15}Sb_{85}$ phase-change films were prepared, using DC sputtering, to study their electrical and optical properties as function of temperature.

2. Experimental

Deposition of $Ge_{15}Sb_{85}$ films was performed by DC sputtering from a composite target in an argon atmosphere of 0.25 pa with a flow rate of 40 sccm (sccm denotes standard cubic centimeter per minute). The amorphous and crystalline natures of the samples were confirmed by X-ray diffraction (XRD) using a Philips PW/1840 XRD with Ni filter and Cu-Kα radiation (λ=1.542A). The composition of the sample was investigated by Energy Dispersive X-ray analysis (EDX), where the measurements confirmed that the film's composition deviate no more than 3% from the composition of the target.

Pre-deposited gold electrodes, 1 mm apart, on glass substrates were used as bottom electrical contacts for resistance-temperature measurement and AC impedance spectroscopy. This configuration has been used to eliminate the effect of electrodes on the electrical properties of the amorphous film [16]. A planar geometry of the film with active area of 1×1 mm^2 was used for electrical measurements, and its thickness is 90 nm. Resistance-temperature measurement (R-T) was performed at temperatures from 300-450 K using electrical heating plate at a heating rate of 10 K/min. The temperature was measured by a K-type thermocouple integrated with the heating plate. The samples were heated in Argon gas environment to avoid oxidation while heating. The impedance spectroscopy measurements were performed using 1260 Solartron impedance analyzer in the range of 1 Hz – 10 MHz, with amplitude of 0.5 volts and zero bias. The optical properties of the film were investigated by studying the transmittance spectra measured using an UV/VIS/NIR spectrophotometer (JASCO 670) in the range of wavelength 200 to 3200 nm (0.39 to 6.2 eV photon energy).

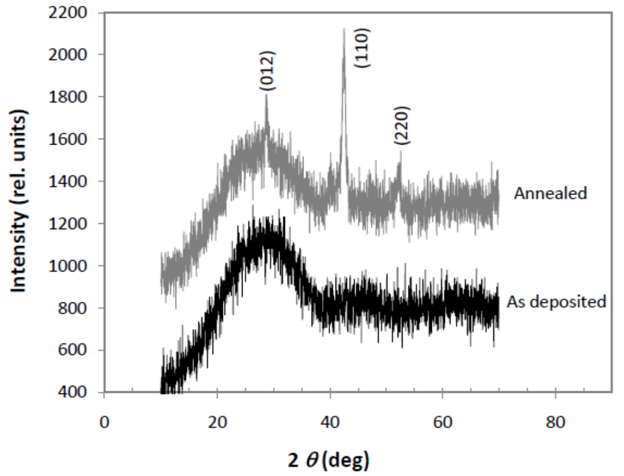

Fig. 1. X-ray diffraction patterns of $Ge_{15}Sb_{85}$ film. a) as-deposited and b) annealed at 450 K for 5 minutes.

3. Results and discussion

The structure of $Ge_{15}Sb_{85}$ films was characterized by XRD. Fig. 1 shows an XRD pattern of the as deposited and annealed films. The smooth pattern signifies the amorphous nature of the as-deposited film. Annealing the film at 540 K for 5 minutes crystallizes it as evidenced by the appearance of sharp peaks in the XRD pattern. The crystalline structure revealed by the XRD pattern is similar to that of pure Sb (Rhombohedral structure). Switching the state of the film to crystalline by temperature is a companied by variation in its electrical properties. The resistance as a function of temperature is shown in Fig. 2. At room temperature the film is amorphous and the measured resistance is high. By increasing the temperature, the resistivity of the film decreases exponentially with an activation energy of about 0.3 eV. An abrupt drop in the resistance is observed at about 420 K. The sharp drop in the resistance indicates amorphous–crystalline phase transition. The critical temperature separating the two states is the crystallization temperature, T_C. The film has a high electrical contrast, with four orders of magnitude difference in resistance between the amorphous and crystalline states. The crystallization temperature of $Ge_{15}Sb_{85}$ alloy has been reported in literature by other authors [17 and 18]. They found that $Ge_{15}Sb_{85}$ alloy has a T_C value of about 500 K. The dissimilarity between the results could be attributed to the differences in the method of deposition (co-sputtering) and heating rate they have used in their study. Our sputtered samples show low T_C of about 420 K which can be attributed to the creation of crystalline channels by annealing as verified by XRD pattern. Consequently, resistance-temperature measurements lead to crystallization temperature similar to that of Sb [18]. Moreover, it is reported that crystallization temperature in Sb rich Ge-Sb films is very sensitive to the stoichiometry of the film; small change in the Sb content leads to a large variation in the crystallization temperature [12].

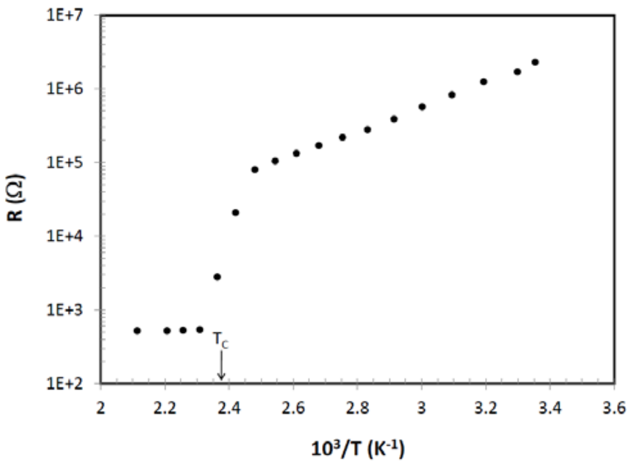

Fig. 2. Resistance as a function of temperature for $Ge_{15}Sb_{85}$ film.

The total impedance of the film can be presented in the form $Z = Z' - jZ''$, where Z' is real part of the impedance representing the resistance of the bulk and Z'' is the imaginary part representing the grain boundary. Materials whose properties are some combination of bulk and grain boundary impedances can be represented ideally by an equivalent circuit consisting of parallel resistor (R) and capacitor (C) elements. Fig. 3 shows the variation of the real part of impedance with frequency at various temperatures. It is observed that the magnitude of Z' decreases with the increase in both frequency as well as temperature, indicating an increase in ac conductivity with rise in temperature and frequency. At zero frequency the Z' values is the bulk resistance R. The inset of Fig. 3 shows the variation of R with temperature. The resistance is thermally activated and decrease with temperature in the form of the expression $R \propto e^{E_v / k_B T}$, where E_v is the activation energy of dc electrical conduction and k_B is the Boltzmann's constant. The value of E_v is calculated from the slope of the straight line fit and found to be 0.3 eV.

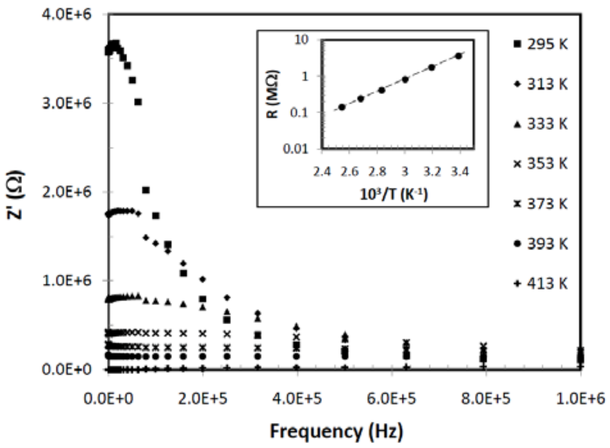

Fig. 3. Variation of real part of impedance Z' with frequency at different temperatures. The inset shows the temperature dependence of the bulk resistance R.

Fig. 4 shows the variation of the imaginary part of impedance Z'' with frequency at different temperatures. The curves show that Z'' values reach a maximum peak ($Z''_{\max}$) for room temperature 295 K and the position of $Z''_{\max}$ shifts to higher frequency with the increase of temperature. This shift in peak maxima with temperature indicates an active conduction through the grain boundary and a decrease in the relaxation of the system. At low frequency and high temperature, the merge of Z'' values is possibly an indication of the accumulation of space charges in the material. Also the curves merge at high frequency and high temperatures.

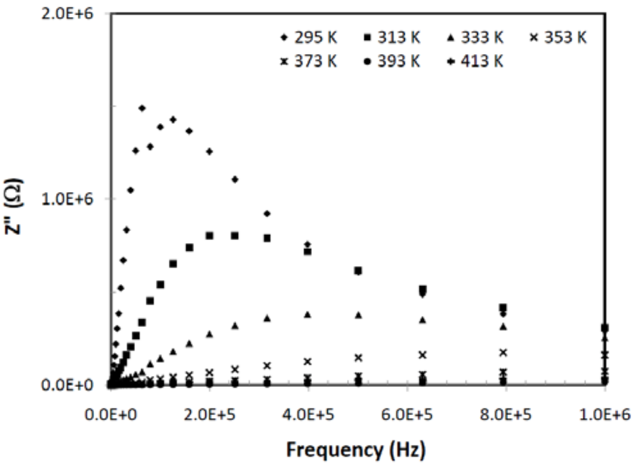

Fig. 4. Variation of imaginary part of impedance Z'' with frequency at different temperatures.

In a relaxation system, the relaxation frequency f_0 can be determined when the bulk resistance, R, and the grain boundary reactance X_C are equal, i.e $2\pi\ f_0 RC = 1$. Fig. 5 shows the frequency dependence of Z' and Z'' at 333 K. When $Z' = Z''$, the relaxation frequency is $f_0 = 5\times10^5$ Hz. The data in Fig. 5 is a representative data on the method to find the relaxation frequency for all temperatures. The relaxation frequency obtained is plotted against the reciprocal temperature as shown in the inset of Fig. 5. It is obvious that the frequency increases exponentially with temperature in the measured range. The value of the activation energy is found to be 0.29 eV. This value is approximately equal to the electrical conduction activation energy calculated from Fig. 3. This connection between the two quantities is in good agreement with literature, where it is reported that semiconductors have similar activation energies for relaxation frequency and electrical conduction.

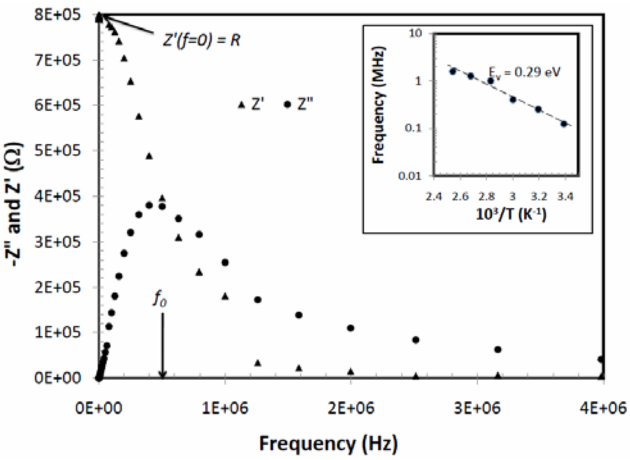

Fig. 5. Frequency dependence of the real and imaginary parts of impedance for $Ge_{15}Sb_{85}$ film at 333 K. The inset shows the relaxation frequency, f versus reciprocal temperature for $Ge_{15}Sb_{85}$ film.

The energy gap and the electronic band structure are significant parameters which identify the electrical and optical proprieties of amorphous semiconductors. Optical transmission and reflection is a valuable method which measures the absorption coefficient α. The absorption coefficient of $Ge_{15}Sb_{85}$ was found to more than 10^4 corresponding to transitions between extended states in the bands, and is characterized by a power law behavior [19] following the relation $\alpha h\nu \propto (h\nu - E_g)^2$, where h is the Plank's constant, ν is the frequency of the absorbed light, and E_g is the optical energy gap. Plotting $(\alpha h\nu)^{1/2}$ versus the photon energy $(h\nu)$ is shown in Fig. 6. The optical energy gap is defined by the intersection of extrapolating the linear portion of the curve with the energy axis at $E_g \approx 0.3 eV$.

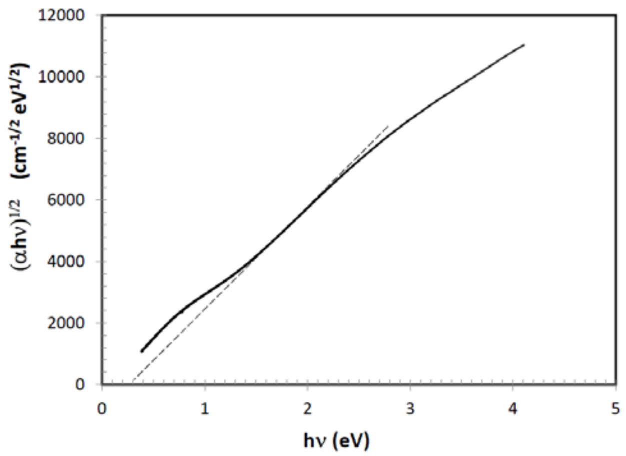

Fig. 6. Plot of $(\alpha h\nu)^{1/2}$ versus photon energy (hν) for $Ge_{15}Sb_{85}$ film. The intercept of dashed line with the energy axis gives the estimated value of the optical energy gap.

In semiconductors, if the electric conduction process is dominated by one type of carriers, the activation energy, E_v, represents the separation of the Fermi energy level, E_F, from the relevant band edge. It is reported that conduction in Ge-Sb films which were deposited at low temperatures is mainly by electrons (n-type) regardless of the Sb content in the film [20, 21]. Thus the activation energy in the present sample ($Ge_{15}Sb_{85}$) represents the location of the Fermi level relative to the conduction band edge E_C such that $E_v = E_C - E_F$. Our result on $Ge_{15}Sb_{85}$ do reflect the presence of the Fermi level in the vicinity of valence band localized tail sates, as evidenced from the comparable estimated values for the optical gap and the electrical conduction activation energies.

4. Conclusions

The electrical and optical properties of tellurium free phase-change material with eutectic alloy of 15% Ge and 85% Sb are investigated. The resistance-temperature measurements show that the crystallization temperature T_C is about 420 K and the material has a high electrical contrast and fast crystallization. XRD shows that annealing a DC sputtered film produce Sb crystalline domains which may be responsible for the lower T_C value than reported in literature. Real and imaginary part of the impedance data demonstrate that $Ge_{15}Sb_{85}$ films can be described as a parallel *RC* circuit, where *R* is bulk resistance of the film and *C* is the grain boundary capacitance. Data analysis show that conduction is thermally activated with activation energy E_v = 0.29 eV. From the transmission and reflection spectra, the optical energy gap E_g was estimated to be 0.3 eV. The similarity $E_v \approx E_g$ predicts that changing temperature shifts the Fermi level in high density valence band tail states.

Acknowledgements

This work is funded by United Arab Emirates University, (grant # FOS/IRG-29/11).

References

[1] S. R. Ovshinsky, Phys. Rev. Lett. 21, 1450 (1968).
[2] T. Ohta, J. Optoelectronics Adv. Mater. **3**, 609 (2001).
[3] E. R. Meinders, A. V. Mijiritskii, L. van Pieterson, M. Wuttig, Optical Data Storage: Phase-change Media and Recording, Philips Research Book Series, 2006.
[4] M. Wuttig, N. Yamada, Nature Mater. **6,** 824 (2007).
[5] M. Lankhorst, B. Ketelaars, R. Wolters, Nature Mater. **4**, 347 (2005).
[6] M. Wuttig, Nat. Mater. **4**, 265 (2005).
[7] N. Qamhieh, S. T. Mahmoud, H. Ghamlouche, J. Optoelectron. Adv. Mater. **9**, 3157 (2007)
[8] R. Neale, D. Nelson, G. Moore Electronics **28**, 56 (1970).
[9] T. C. Chong, L. P. Shi, Appl. Phys. Lett. **88**, 122114 (2006).
[10] S. Lai, IEDM Tech. Dig. 255, 2003.
[11] C. W. Jeong et., al., Jpn. J. Appl. Phys. **45**, 3233 (2006).
[12] D. Kerbs, S. Raoux, C. T. Rettner, R. M. Shelby, G. W. Burr, M. Wuttig, Mat. Res. Soc. Proc. **1072**, 2008.
[13] T. Zhang, Z. T. Song, F. Wang, B. Liu, S. L. Feng, B. Chen, Appl. Phys. Lett. **91**, 222102 (2007).
[14] T. Zhang, Z. T. Song, B. Liu, S. L. Feng, Semicond. Sci. Technol. **23**, 055010 (2008).
[15] J. Hegedus, S. R. Elliott, Phys. Status Solidi A **207**, 510 (2010).
[16] S. T. Mahmoud, H. Ghamlouche, N. Qamhieh, H. Al-Shamisi, Appl. Surf. Sci. **253** 7242 (2007).
[17] Yifeng Gu, Ting Zhang, Z. Song, Y.Liu, Bo Liu, S. Feng Appl. Phys. A **99**, 205 (2010).
[18] D. Kerbs, S. Raoux, C. T. Rettner, G. W. Burr, R. Shelby, M.Salinga, C. Jefferson, M. Wuttig J. App. Phys. **106**, 054308 (2009).
[19] J. Tauc, Amorphous and liquid Semiconductors, Plenum Press, New York, 1974.
[20] G. M. Beensh-Marchwicka, W. Mielcarek, E. Prociow, Sensors and Actuators B **76**, 361 (2001).
[21] D. Krebs, PhD Thesis, RWTH – Aachen, Germany, 2010.

*Corresponding author: saleh.thaker@uaeu.ac.ae