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ELECTRICAL PROPERTIES OF $In_{0.3}Ge_2Sb_2Te_5$ FILMS USING IMPEDANCE SPECTROSCOPY

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The influence of indium doping on the electrical properties of $Ge_2Sb_2Te_5$ is investigated. Amorphous $Ge_2Sb_2Te_5$ and $In_{0.3}Ge_2Sb_2Te_5$ films were prepared by thermal evaporation technique. The relaxation frequency and capacitance as a function of temperature are analyzed using impedance spectroscopy measurements. From this analysis, it is found that adding indium reduces the activation energy of the $Ge_2Sb_2Te_5$. The capacitance increases for $Ge_2Sb_2Te_5$ sample while it decreases for the $In_{0.3}Ge_2Sb_2Te_5$ as the temperature approaches the amorphous-crystalline transition. The results indicate that Indium plays an important role in modifying the electrical properties of $Ge_2Sb_2Te_5$ phase-change materials.

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Keywords: Impedance Spectroscopy; Amorphous Films; Phase-Change; Ge-Sb-Te

1. Introduction

Amorphous chalcogenide thin films have become increasingly important and attracted much attention as a new advanced and replaceable technology material because of their electrical, optical and thermal properties, including the change of the electric resistance and the optical reflectivity [1-4]. The interest in the study of Ge:Sb:Te alloys is due to their use as active materials in optical and electronic devices. The application of these devices is based on the ability of these materials to be reversibly transformed between amorphous and crystalline phases; this results in changes in their optical and electrical properties [5-9]. Recently these materials have enabled the development of phase-change random access memories (PRAMs), which are promising nonvolatile memory device [10]. $Ge_2Sb_2Te_5$ is the most widely used composition. Up to now, the search for recording materials possessing fast crystallization rate and long data retention has been pursued. To meet both requirements, efforts have been made by using the chemical modification approach [11]. In related studies, transition metals such as Co, Ti, and Ag were introduced into $Ge_1Sb_2Te_4$ or $Ge_2Sb_2Te_5$ to improve the carrier-to-noise ratio and lifetime of the recorded bits [12, 13]. It was reported that doping with oxygen and /or nitrogen improves the recording sensitivity, erasibility, and overwriting of $Ge_2Sb_2Te_5$ alloys [14-16]. The influence of indium doping on the crystallization kinetics of $Ge_2Sb_2Te_5$ has been investigated by Wang *et al*., [17]. The results indicate that indium might play an important in modifying the crystallization kinetics of Te-based phase change materials.

In this work, the electrical characterization of indium-doped $Ge_2Sb_2Te_5$ phase-change material has been investigated using impedance measurements. Comparison between $In_{0.3}Ge_2Sb_2Te_5$ and $Ge_2Sb_2Te_5$ films is presented.

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2. Experimental

Two thin film samples (S1 and S2) of $Ge_2Sb_2Te_5$ were prepared at the Physics Institute (RWTH, Aachen, Germany). The samples S1 and S2 have coplanar and sandwich configurations, respectively. A third sample (S3) of $In_{0.3}Ge_2Sb_2Te_5$ is prepared in our lab by melt quenching technique. Materials (99.995% pure) are weighed according to their atomic percentage and sealed in quartz ampoules in a vacuum $\sim 10^{-3}$ mbar. The sealed ampoule is kept inside a rotating cylindrical furnace at 1050°C for 24 hours to make the melt homogeneous. Thereafter, the quenching is done in ice-water bath. Thin film sample (S3) is prepared by thermal evaporation at a base pressure of 1×10^{-5} mbar. The amorphous nature of these films is confirmed by X-ray diffraction (XRD). The compositions of the evaporated samples are measured by Energy Dispersive X-ray analysis EDX. Pre-deposited thick gold electrodes on glass substrates are used for the electrical contacts as shown in Fig. 1. This configuration has been used to eliminate the effect of electrodes on the electrical properties of the thin film [18].

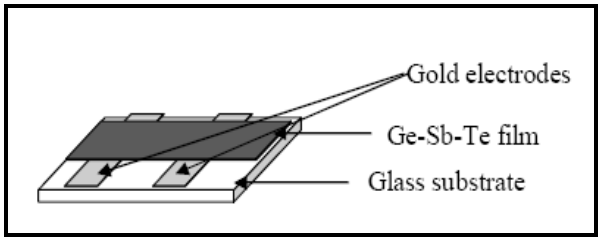
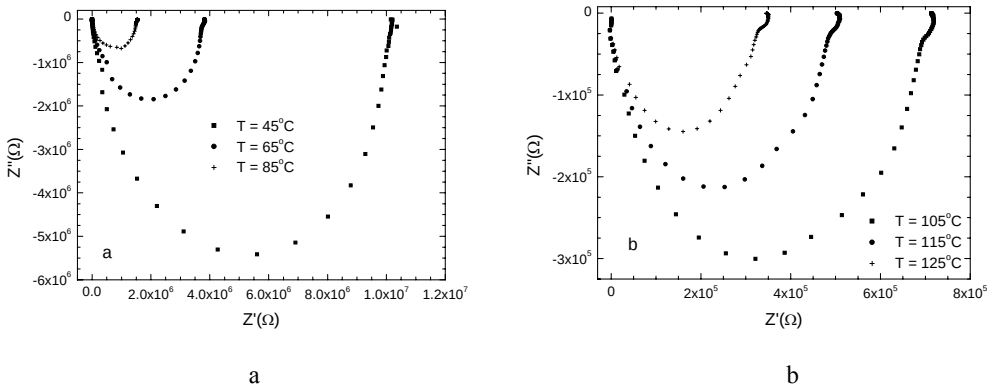


Fig. 1. Schematic diagrams of the electrical contacts. The gold electrodes are evaporated on a glass substrate and then the film is deposited.

Two gold electrodes were used for the AC impedance spectroscopy. The impedance spectroscopy measurements were performed using 1260 Solartron impedance analyzer in the range of 1 Hz–10 MHz, with amplitude of 0.5 V and zero bias. Silver paste has been used to make contact between the coaxial cable and the gold electrodes. The measurements were performed at different temperatures using electrical heating board kept inside a faraday cage. The samples were heated in Argon gas environment. The temperature was measured by a K-type thermocouple built in the heating board.

3. Results and discussion

Figs. 2, 3 and 4 show the impedance spectra (Nyquist plot) at different temperatures of samples S1, S2 and S3, respectively. The impedance spectra is the plot of imaginary part of the impedance Z" versus its real part Z′. It can be observed that at certain temperature, the distribution of frequencies fit with one semicircle in samples S2 and S3 (Figs. 3 and 4), whereas, in the case of sample S1 another small semicircle is observed at low frequencies. This can be related to the to contact effect, since the configuration shown in figure 1 has been used for samples S2 and S3 while for sample S1 the electrodes are evaporated directly on the top of the film. The presence of the small semicircle had been observed by Morales-Sanchez *et al*., [19]. They claimed that at temperatures between glass transition temperature (T_g) and amorphous-crystalline transition temperature (T_C), a mixture of two phases: amorphous and crystalline nuclei are formed.



a b

Fig. 2. Impedance spectra for $Ge_2Sb_2Te_5$ film using coplanar sample. The measurements were taken at temperatures of: a) 45 °C, 65 °C, 85 °C, b) 105 °C, 115 °C and 125 °C.

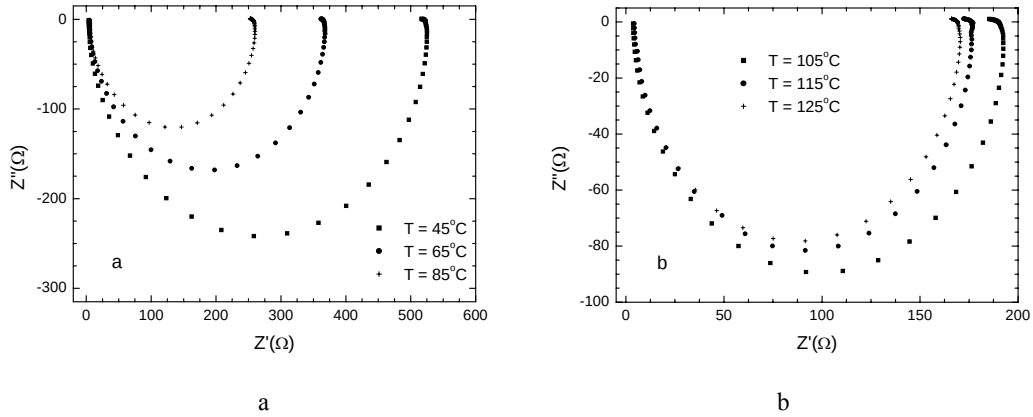


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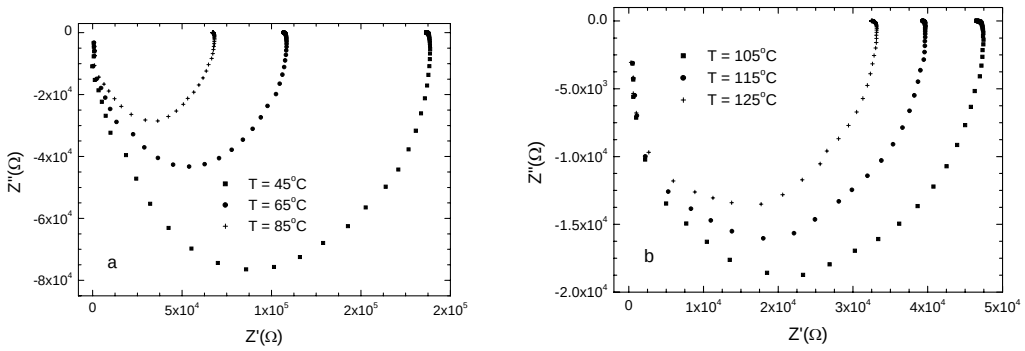
Fig. 3. Impedance spectra for $Ge_2Sb_2Te_5$ film using sandwich sample. The measurements were taken at temperatures of: a) 45 °C, 65 °C, 85 °C, b) 105 °C, 115 °C and 125 °C.

It is obvious from Figs. 3 and 4 that only one semicircle is observed in samples 2 and 3. Despite its existence, the nucleation process is hard to be detected using impedance spectroscopy technique. However, in sample 1 the second semicircle can not be attributed to nucleation effect since it is observed at low temperatures and not only between T_g and T_C.

As expected, in Figs. 2, 3 and 4, the diameter of the semicircle keeps decreasing with increasing the temperature. Moreover, the semicircle peak shifts toward higher frequency as the temperature increases. A parallel resistor and capacitor (RC) equivalent circuit accurately fit the frequency data [20]. Hence the electrical properties of the films can be associated to a simple RC equivalent circuit. R is determined from the diameter of the semicircle and C is determined by using the frequency at the peak of each semicircle (relaxation frequency, *f*), where $2\pi\ fRC = 1$ should be satisfied.



a b

Fig. 4. Impedance spectra for $In_{0.3}Ge_2Sb_2Te_5$ film using coplanar sample. The measurements were taken at temperatures of: a) 45 °C, 65 °C, 85 °C, b) 105 °C, 115 °C and 125 °C.

The relaxation frequency (f) obtained is plotted against the reciprocal temperature for all samples, as shown in Fig. 5. It is obvious that the relaxation frequency is thermally activated according to the Arrhenius relation.

$$f \propto e^{-E_v / k_B T}, \tag{1}$$

where E_v, is the activation energy and k_B is Boltzmann's constant. From figure 5 the frequency increases exponentially in the measured temperature range. The activation energies for samples S1, S2 and S3, calculated from the slope of the straight line fit, are found to be E_{v1} = 0.43 eV, E_{v2} = 0.16 eV and E_{v3} = 0.25 eV, respectively.

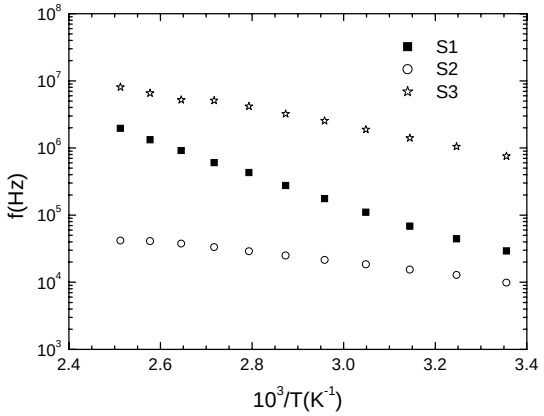


Fig. 5. Relaxation frequency, f versus reciprocal temperature for samples S1, S2 and S3.

The activation energy (E_{v1} = 0.43 eV) of sample 1 that has a coplanar configuration is very close to values reported in literature [10]. However, the value of activation energy (E_{v2} = 0.16 eV)

of sample 2 that has sandwich configuration is relatively small. This could be attributed to the diffusion of the electrodes' materials into the surface of the film. It is well known that doping Ge-Sb-Te films with metals reduces the activation energy [21]. Therefore, the activation energy of sample S3 that is doped with indium is smaller than the activation energy of the undoped sample S1.

Fig. 6 shows the variation of the normalized capacitance $C/C_{25^\circ C}$ as a function of temperature for the three samples. $C_{25^\circ C}$ is the capacitance at room temperature. It is obvious that $C/C_{25^\circ C}$ increases for S1 and S2 and decreases for S3 as the temperature increases.

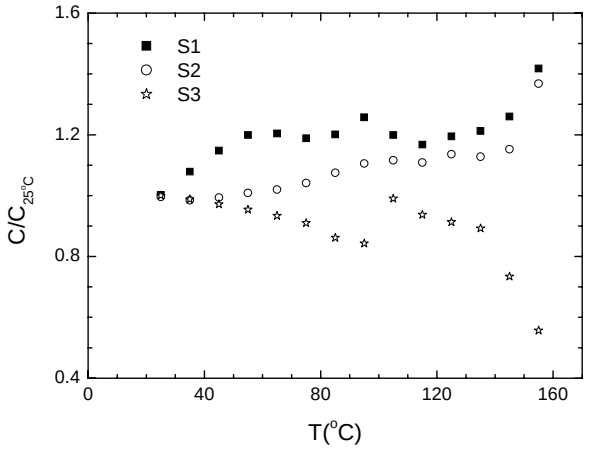


Fig. 6. Normalized capacitance, $C/C_{25^\circ C}$ versus temperature for samples S1, S2 and S3.

The dependence of the capacitance on temperature and frequency has been previously explained in terms of the equivalent circuit model [22, 23]. This model comprises a frequency and temperature-independent capacitive element C' in parallel with a discrete temperature dependent resistive element R (due to the film). These two elements (R and C') are in series with a constant low value resistance (due to electrical contacts). According to this model the measured series capacitance is given by:

$$C = C' + \frac{1}{\omega^2 R^2 C'} \tag{2}$$

The resistive element R, assumed to be thermally activated with temperature variation, is given by:

$$R = R_0 e^{E_v / k_B T}, \tag{3}$$

where R_0 is a pre-exponential constant. Equation (2) clearly predicts that the measured capacitance decreases with increasing frequency, eventually at high frequencies becoming frequency-independent and reaching the constant value C'. For a given frequency the capacitance will increase with increasing temperature, since R decreases with increasing temperature according to the well known activation process of equation (3). This effect is qualitatively evident in figure 6 for samples S1 and S2. Holes are the main carriers that are responsible of electrical transport in these two samples (i.e. p-type semiconductor) [10]. When Ge-Sb-Te material is doped with indium (S3) both carriers (electrons and holes) are responsible of electrical transport. The capacitance variation with temperature is governed by the comparison between the reactive component of current and the Maxwellian displacement current provided the DC conductivity is inertial as detailed below [24].

In the case of application of an alternating voltage across certain semiconducting material, the equivalent capacitance measured is given by [25]:

$$C_e = (\frac{A\sigma_{DC}}{d})[\tau_m - \frac{\tau}{1+\omega^2\tau^2}] \quad (4)$$

Here, A is the area of the plate capacitor and d is the dielectric thickness. $(\tau_m = \frac{\varepsilon}{4\pi\sigma_{DC}})$ is the Maxwellian dielectric relaxation time, τ is the dielectric relaxation time, ε is the dielectric constant and σ_{DC} is the DC conductivity. The decrease in C appears when τ_m decreases. For the doped sample with indium, the concentration of free electrons is higher than undoped samples. Moreover, as the temperature increases the electrons concentration increases furthermore. Therefore the DC conductivity σ_{DC} increases and hence the Maxwellian dielectric relaxation time τ_m decreases.

4. Conclusions

The electrical properties of indium doped $Ge_2Sb_2Te_5$ alloy using impedance spectroscopy have been investigated. The data has shown similar behavior of resistance and relaxation frequency temperature dependence. The activation energies estimated from the relaxation frequency curves as a function of reciprocal temperature are 0.43 eV and 0.25 eV, for $Ge_2Sb_2Te_5$ and $In_{0.3}Ge_2Sb_2Te_5$, respectively. The effect of temperature on the normalized capacitance $C/C_{25\,^\circ C}$ has been investigated. The normalized capacitance $C/C_{25\,^\circ C}$ increases for undoped samples while it decreases for doped sample as the temperature approaches the amorphous-crystalline transition (T_C). The capacitance variation with temperature is governed by the comparison between the reactive component of current and the Maxwellian displacement current. The results show that indium plays an important role in modifying the electrical properties of $Ge_2Sb_2Te_5$ materials.

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