JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 6, June 2008, p. 1448 - 1451

Steady-state photoconductivity in amorphous $Ge_2Sb_2Te_5$ films

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Steady-state photoconductivity measurements are carried out on thermally evaporated thin films of amorphous $Ge_2Sb_2Te_5$ samples in the temperature range between 323 and 243 K. The temperature dependence of the photoconductivity ensures the absence of the maximum normally observed in chalcogenides, and the photocurrent is thermally activated with activation energy slightly lower than that of the dark current value, 0.22±0.02 eV. The measured activation energies suggest recombination dominated by a trap states located at the equilibrium Fermi energy level. In the low temperature range another defect level corresponds to a deep electron trap carrier transport can be suggested which leads to low-temperature sensitisation of the photocurrent. The latter is evidenced from the γ values of approximately 1.0 in the Lux-Ampere characteristics.

(Received May 5, 2008; accepted June 4, 2008)

Keywords: Phase change materials, Density of states, Defects, Photoconductivity, Chalcogenides

1. Introduction

Phase change materials based on chalcogenide alloys are found to be suitable for optical and electrical memories due to their fast crystallization. The operation principle of these devices is based on the ability of the active materials to reversibly transform between amorphous and crystalline phases. Among these alloys, $Ge_2Sb_2Te_5$ exhibits the best performance when used in DVD-RAM in terms of speed and stability [1,2]. This alloy ($Ge_2Sb_2Te_5$) demonstrates high thermal stability at room temperature, high crystalline rate at high temperatures (can be crystallized by a less than 50 ns laser pulse), and extremely good reversibility between amorphous and crystalline phases (more than 10^5 cycles) [3]. In the last few years, these materials have been extensively studied to understand the crystallization phenomena [4-11]. The rapid and reversible amorphous-to-crystalline phase transformation is accompanied by increase in the optical reflectivity and the electrical conductivity. The common feature of these glasses is the presence of localized states in the mobility gap. The optical properties of amorphous films of $Ge_2Sb_2Te_5$ depend strongly on the preparation conditions, and concequently on the defects presented in the energy gap [12], which determine many of the electrical properties of amorphous semicondcutors [13].

Photoconductivity gives information about defect states as recombination centers. In chalcogenides, these centers are the defects with negative effective correlation energy (negative-U model [14]). These defects produce discrete energy levels in the gap of amorphous chalcogenide semiconductors [13]. Consequently, steady-state photoconductivity is a valuable technique to identify the position of these levels. The dependence of photocurrent on temperature and on intensity of illumination allows identification of areas with monomolecular or bimolecular recombination behavior. At high temperatures and low light intensities, where monomolecular recombination dominates, the photocurrent is positively activated with the reciprocal temperature, while at lower temperatures and high intensities bimolecular recombination leads to a different and negative value of the activation energy. In terms of the activation energies in the two regimes the quantities of discrete trapping levels in the gap can be specified [15, 16]. The two regimes have been observed on a large number of amorphous semiconductors [17 - 21].

In the present work, steady-state photoconductivity measurements on amorphous $Ge_2Sb_2Te_5$ films have been investigated. The temperature dependence of dark- and photo- currents, besides the photocurrent behaviour at different light intensities has been examined.

2. Experimental

Thin films (about 1μm thick) were prepared by thermal evaporation onto glass substrate of melt-quenched glasses of the $Ge_2Sb_2Te_5$. Evaporated gold electrodes on top of the films made gap cells with active areas of 0.5×10 mm^2. X-ray examination of several films proved that they were fully amorphous.

DC conductivity measurements were carried out in a 5×10^{-3} Pa atmosphere by means of a Keithley 427 current amplifier, with 10 V applied across the gap. He-Ne laser was used for gap cell illumination with 1.96 eV light energy. Calibrated neutral density filters served to modify the light intensity. Photocurrents were monitored by connecting the Keithley current amplifier to a digital multimeter, or to a strip chart recorder for studying the (slow) time evolution of the currents. For steady-state photoconductivity (SSPC) measurements, the sample is placed on a metal support in the vacuum chamber. The sample's temperature is controlled by a combination of liquid nitrogen cooling and regulated electrical heating of the sample holder.

3. Results

Fig. 1 shows the temperature dependence of the dark- and photo-currents of the $Ge_2Sb_2Te_5$ film in the temperature range of 323–243 K. The measured dark current is relatively high in comparison with other chalcogenides (Se, AsSe etc.), due to its small energy gap. An Arrhenius plot of the conductivity in figure 1 shows that the dark current is more or less linear, indicating that the conduction in these glasses is through an activated process having a single activation energy of 0.22 ± 0.02 eV in the investigated temperature range. The photocurrents are two decades smaller than the dark current. The photo-current maximum, which is a common feature of the chalcogenide glasses [17-21], is absent. Above 280 K ($10^3/T < 3.6K^{-1}$) the measured photo-current simply decreases slowly and monotonically with decreasing temperature. To first approximation, it can be described by the thermally activated process with activation energy slightly lower than that for the dark current, which normally governs the bimolecular recombination at the low temperature end in chalcogenides. At temperatures below 280 K, the photo activation energy reduced to a smaller value.

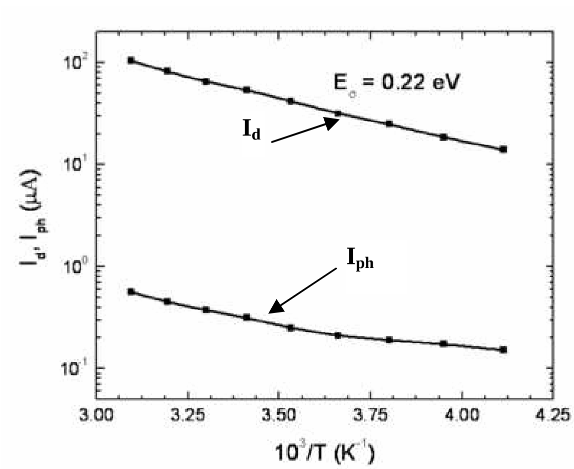

Fig. 1. Temperature dependence of the dark current (I_d) and photocurrent (I_{ph}) of $Ge_2Sb_2Te_5$ film illuminated with 15 mW He-Ne laser. Solid lines are to guide the eye.

An important and useful parameter in photoconductivity measurements is the photosensitivity (I_{ph}/I_d) at a particular temperature. Using the results in Fig.1, the values of the photosensitivity as a function of reciprocal temperature are plotted in Fig. 2. The increase in the photosensitivity is obvious in this figure as usually observed in chalcogenides [17-21]. Although both photocurrents and dark currents are decreasing with reciprocal temperature (Fig. 1); the rate in the photocurrent change is less than that for the dark current, above 3.6 K^{-1} the decrease in the photocurrent is slower than the dark current. This would lead to a significant increase in the photosensitivity in Fig. 2. A similar phenomenon was observed in SSPC in amorphous Se and $Se_{85}Te_{15-x}Pb_x$ thin films [22, 23] encountered at low temperatures, which was interpreted in terms of photosensitisation.

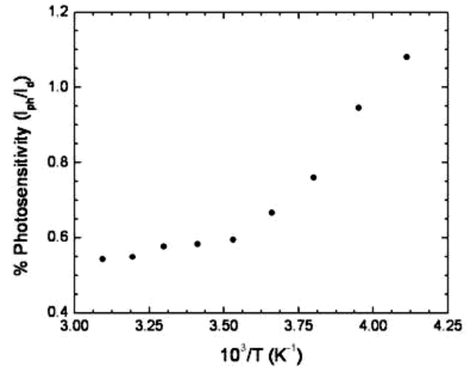

Fig. 2. Temperature dependence of the photosensitivity (I_{ph}/I_d) of $Ge_2Sb_2Te_5$ film.

Experimental evidence for photosensitisation in $Ge_2Sb_2Te_5$ is gained through the light intensity dependence of the photocurrents (Lux-Ampere characteristics), this has been investigated at different temperatures. Fig. 3 shows the photocurrent induced by 1.96 eV illuminations as a function of light intensity, I, over three orders of magnitude at three different temperatures, 243, 303, and 323 K. It is clear that the photocurrent, I_{ph}, at all temperatures grows approximately linearly with light intensity, I, and hence photo-carrier generation rate G, according to the formula $I_{ph} \propto G^{\gamma}$, where γ has values of approximately 1.0.

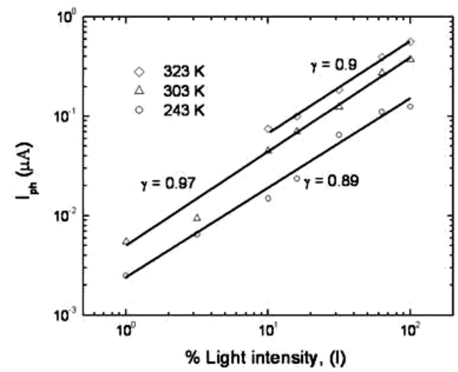

Fig. 3. Lux-Ampère characteristics of $Ge_2Sb_2Te_5$ film illuminated with 15 mW He-Ne laser at different temperatures. Solid lines are to guide the eye

4. Discussion

If the electric conduction process in $Ge_2Sb_2Te_5$ is dominated by one type of carriers, E_σ in Fig. 1 represents, to first order, the separation of the Fermi energy level from the relevant band edge. Hall measurements showed that $Ge_2Sb_2Te_5$ is highly p type [24, 25], which is the general conduction type in chalcogenides. Thus the activation energy in the present sample approximates the location of the Fermi level, E_F, relative to the valence band edge. In general E_F in chalcogenides is located near the middle of the gap (i.e. $E_\sigma \approx 0.5\ E_g$) [26]. The measured activation energy of about 0.22 eV indicates that the mobility gap is approximately 0.44 eV which is smaller than the reported optical gap value (≈ 0.7 eV) measured for sputtered $Ge_2Sb_2Te_5$ films [24]. Here if we take into consideration the chalcogenide character of $Ge_2Sb_2Te_5$ (p type conduction), the Fermi level is located somewhat closer to the valence band edge than to the conduction band edge. This certainly leads to a mobility gap greater than 0.44 eV.

The temperature dependence of the photocurrent (Fig. 1) differs from that found in most of other amorphous chalcogenides. In the latter the charged negative-U defects govern the recombination and lead to decreasing photocurrents, at both high and low temperatures, with activation energies that are much below the one for the dark current [26]. The poor photosensitivity in (Fig. 2) makes the photoconductivity method described above unable to provide enough information on possible presence of discrete defect levels in the band gap of $Ge_2Sb_2Te_5$ samples. However, the data in Fig. 1 suggests recombination dominated by a trap states [27], which should be located near the Fermi energy level in view of the closeness of photo- and dark currents activation energies. The decrease in the photo-activation energy was related to the photothermal-conductive process [28]. To minimize any photothermal contribution, the glass substrate, upon which the amorphous sample was deposited, was mounted on a copper heat sink with an integrated heater and a thermocouple. The heat sink allows nitrogen to flow through it and maintains a constant temperature for the sample. Therefore, we suggest that the observed photoconductivity spectrum below 280 K presented in Fig. 1 is due to photosensitization.

Photosensitivity is to some extent the counterpart of the negative photoconductivity described by A. Rose [29]. Here it is required that the changes in the illumination intensity or the temperature move the quasi-Fermi level for the majority carrier past a specific trapping level that has a large capture probability for the minority carrier, combined with a very small capture probability for the majority carrier. Recombination of the majority carrier then becomes less probable, with an enhanced photocurrent as a consequence. The occurrence of photo-sensitisation (and hence the action of a discrete trapping level with the required characteristics) can be deduced from changes in the characteristic exponent γ of the Lux-Ampère relationship between photocurrent and light intensity $I_{ph} \propto G^{\gamma}$. In chalcogenides, the values of γ will normally vary from 1.0 in the monomolecular recombination regime at high temperature to 0.5 at low temperature where recombination becomes bimolecular. In Fig. 3, γ values of approximately 1.0 at low temperatures are sign for photosensitisation, and consequently the data suggest a discrete defect level in the band gap of amorphous $Ge_2Sb_2Te_5$ film.

5. Conclusion

Steady-state photoconductivity is a valuable technique to study the defect levels in the gap of amorphous semiconductors. Measurements on thermally evaporated $Ge_2Sb_2Te_5$ films were unable to resolve the discrete levels of the negative-U defect, which are confirmed in other chalcogenides. Nevertheless, two unrelated electron traps can be evidenced. A deep electron trap is deduced in the vicinity of the equilibrium Fermi energy level at E^*-E_v = (0.22 ± 0.02) eV in view of the closeness of photo- and dark current activation energies. For temperatures below 280 K, sensitisation of the steady-state photocurrent implies the presence of defects with capture cross section for charge carriers different from other localized gap states.

Acknowledgements

N.Q. and M.L.B. are grateful to Semiconductor Physics group at the University of Leuven for hospitality and fruitful discussion during their summer stay. This work was financially supported by the Research Affairs at the UAE University under grant no. 03-02-2-11/08.

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