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# Phase transition of gallium containing telluride thin films♣

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The phase transition of thin $(GeTe_5)1\text{-}xGa_x$ films has been investigated using the temperature dependent sheet resistance method. The dependence of the resistance upon the gallium content and temperature has been discussed. The films with the highest gallium content of 20 mol.% exhibit two transitions in the sheet resistance at 90°C and 250 °C, where the sheet resistance changes by 3 orders of magnitude.

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*Keywords*: Chalcogenide glasses, Thin films, Sheet resistance

## 1. Introduction

Tellurium-based chalcogenide glasses attract strong scientific and commercial interest, because of their valuable optical features. They have been intensively studied in respect of their infrared transmission abilities [1], for use in optical memories and optical data storage [2], particularly those Te-based optical glasses that are stable enough against crystallization to allow the manufacturing of bulk optics.

In addition to the interest in the applications of the chalcogenide glasses in optics and telecommunications, their structural and thermal properties have also been the subject of research investigations [3]. The introduction of metal atoms into a chalcogenide matrix is often used to vary the optical and thermal properties in a desired direction [4].

Recently, a paper has been published devoted to the Ge-Te-Ga glasses, where a strategy for the fabrication of a flexible glassy network, keeping a high content of Te, has been reported with a view to obtaining vitreous materials having an IR cut-off shifted towards long wavelengths [5].

In this work, we investigate thin films in the $(GeTe_5)_{100-x}Ga_x$ system, using a temperature dependent van der Pauw method to establish the effect of Ga addition on the crystallization kinetics of $GeTe_5$ alloys.

## 2. Experimental

Bulk chalcogenide glasses from the ternary $(GeTe_5)_{100-x}Ga_x$ (x = 5, 10, 15, 20 at%) system were prepared from the starting elements with 5N purity, by direct mono-temperature synthesis in evacuated ($1.33x10^{-3}$ Pa) quartz ampoules. The final temperature of the synthesis, of 1300 K, was kept constant for 48 hours. The melts were quenched at a rate of about 150 $Ks^{-1}$, in a mixture of water and ice.

Thin films were deposited by thermal evaporation from the corresponding bulk glasses, in a conventional vacuum set-up with a residual gas pressure of $1.33x10^{-4}$ Pa, a source-substrate distance of 0.12 m, and a maximum evaporation temperature between 700 and 800 K, depending on the glass composition. Due to the different partial pressures of the components constituting the vapor phase, the thin films were deposited from a quasi-closed tantalum evaporator with direct heating [6]. Various substrates suitable for different experiments and analyses were used: monocrystalline Si wafers, NaCl and optical glass. They were rotated during the deposition to avoid thickness non-uniformity in the coatings. The film thickness measured by means of an interferometer was between 70 and 500 nm, depending on the experimental purposes.

After deposition, the $(GeTe_5)_{1-x}Ga_x$ films were characterised with respect to their structure, composition,

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morphology, growth rate and topography, in order to elucidate the influence of the glass composition on their behaviours. The structures were studied by X-ray diffraction (XRD), using a Philips MRD system with $CuK_\alpha$ excitation radiation. We worked in a θ - 2θ configuration within the range 20° - 65°, with a step of 0.05° and acquisition time 2 s. The film morphologies and structures were studied by transmission microscopy in the normal mode and diffraction mode respectively. A "TEM-400 Phillips" instrument with a magnification of $2.10^4$ was utilized.

The sheet resistance study were carried out based on the the Van der Pauw approach. The method allows the observation of the phase transition as a function of the temperature and composition. The temperature of the phase transition was determined from the minimum in the sheet resistance versus the crystallization temperature of the alloy.

## 3. Results and discussion

### 3.1. Structure study

The films, as deposited, were amorphous. This assertion has been verified by two independent methods – TEM and XRD.

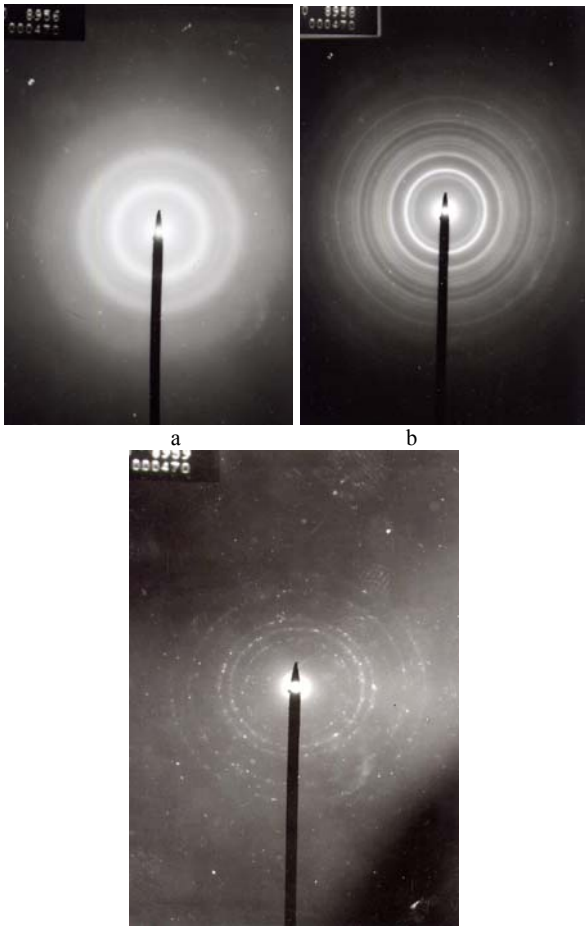


*Fig. 1. Electron diffraction patterns of the $Ge_{13}Te_{67}Ga_{20}$ film as deposited (a), after annealing at 90 °C (b) and 150° C (c).*

The electron diffraction pictures in Figs. 1 a - c, demonstrate the changes in the film structure due to the temperature. The as deposited film was amorphous, from the halo in Fig. 1a. The higher the annealing temperature, the more visible were the diffraction rings in Figs. 1b and c. The amorphous nature of as deposited films has been also shown by the X-ray studies. The broad halos in Fig. 2 indicate the non-crystalline character of the films, and the absence of crystalline inclusions. Crystalline phases in the $Ge_{13}Te_{67}Ga_{20}$ film are not detected upon annealing either at 90° or 150°C, as seen from Figs. 1b and c. A further increase in the annealing temperature to 250°C causes the appearance of sharp peaks; a sign for the crystallization of the $Ge_{13}Te_{67}Ga_{20}$ alloy (Fig. 3).

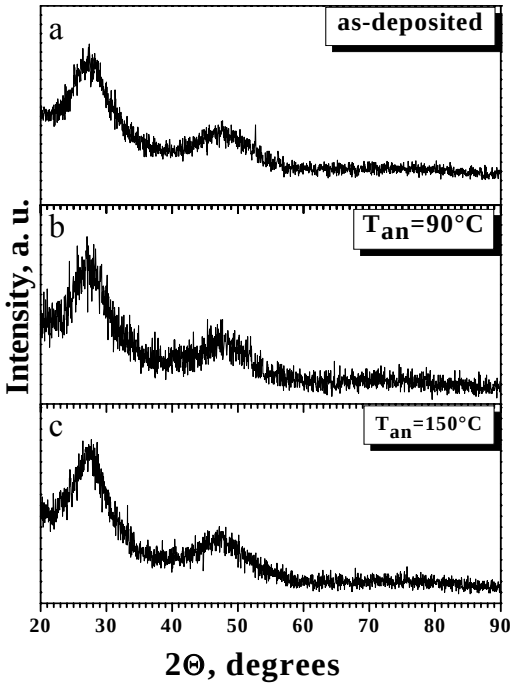


*Fig. 2. XRD spectra of the $Ge_{13}Te_{67}Ga_{20}$ alloy as deposited curve (a), after annealing at 90°C (curve b) and 150° C (curve c), respectively.*

The analysis of the phases revealed the existence of stable binary GaTe and $Ga_2Te_3$ phases. Surprisingly, the binary GeTe phase was not detected, while a complex phase of GaGeTe was distinguished, as shown on the diffractogramme. For the GaGeTe phase, a rhombo-centred hexagonal lattice was identified and the corresponding lattice parameters were determined to be a = b = 3.967 ± 0.003 Å and c = 33.773 ± 0.029Å. These values are in agreement with those given by Fenske et al. [7]. Similar calculations for the GaTe sample yielded a

monoclinic structure with lattice parameters a = 17.355 ± 0.024 Å, b = 10.442 ± 0.014 Å and c = 4.069 ± 0.024 Å, respectively, after identifying the Bragg reflexes using the PDF card [8]. In addition, the $Ga_2Te_3$ phase was also identified in the XRD spectrum and it is attributed to a face centred cubic structure with lattice parameters a = b = c = 5.886 ± 0.003 Å [9].

### 3.2. Temperature dependent sheet resistance measurements.

Temperature dependent sheet resistance measurements have been performed to establish the effect of Ga addition on the transition

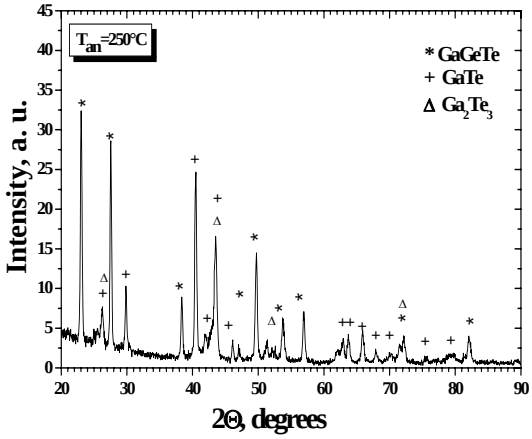


*Fig. 3. Diffractogramme of the $Ge_{13}Te_{67}Ga_{20}$ film annealed at 250°C.*

temperatures of the $GeTe_5$ binary alloys. In all films, the resistance was found to decrease as the temperature increased.

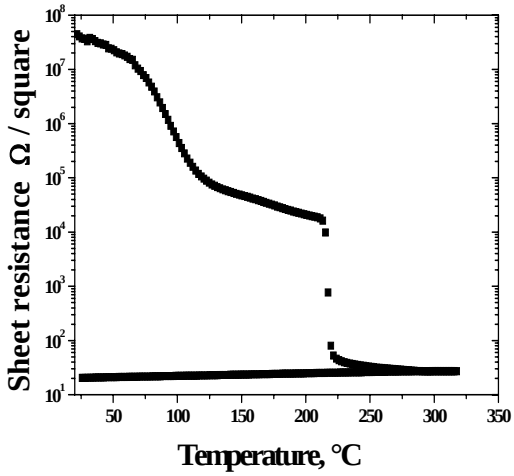


*Fig.4. Temperature dependent sheet resistance measurements for the $Ge_{13}Te_{67}$ $Ga_{20}$ film.*

The sheet resistance as a function of the temperature of a $Ge_{13}Te_{67}Ga_{20}$ thin film is shown in Fig.4. The continuing decrease in the resistance is interrupted by two sharp drops in the sheet resistance, observed in the $Ge_{13}Te_{67}Ga_{20}$ composition only.

The first transition in the sheet resistance, that occurs at the lower temperature, is defined by a two orders of magnitude decrease in the resistance values. The relatively low temperature of the first transition (at about 90°C) suggests that the transition is not assigned to film crystallization. Most probably, a structural transformation takes place related to the structural arrangement, which bring about a tightening of the film packing.

The second sharp transition in the sheet resistivity values can be attributed to an amorphous - crystalline transition. This has been observed in similar tellurium containing chalcogenide alloys, and already reported by some of our team [10-12].

The reversibility of the first transition has been studied by performing sheet resistance measurements up to the region just before the onset of the second transition. The results of the experiment are presented in Fig. 5.

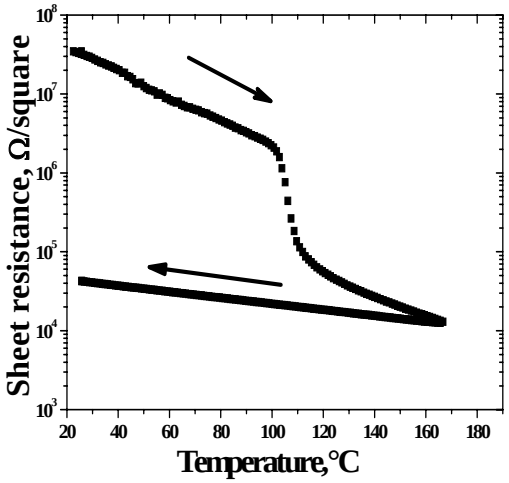


*Fig. 5. Irreversibility of the first transition of the $Ge_{13}Te_{67}$ $Ga_{20}$ film.*

The trend of the resistivity dependence was changed once the transition was achieved and the temperature was lowered. The transition initiates an irreversible change in the sheet resistance, most probably associated with relaxation of the amorphous phase and changes in the constitution of the amorphous phase, like rearrangement of the bonds and bonding angles in the glassy matrix.

Corroboration of this suggestion is provided by the XRD study data and TEM measurements discussed in the previous section.

### 3.2. Study of the film behaviors under annealing, depending on concentration of gallium.

The effect of Ga addition on the transition temperatures of the $GeTe_5$ binary alloys was investigated, and the results of these measurements are presented in Fig.

6. It is evident that Ga addition leads to an increase in the transition temperature, by approximately 19 %.

Studies by Petkov et al. [13] of the effect of Ga on $(GeTe_5)_{100-x}Ga_x$ bulk samples, using DSC experiments, have shown a 13% increase in the crystallization temperature for up to 15 % Ga compositions.

The results obtained could be explained in terms of structural arrangement. We suppose that Te-rich Ge-Te alloys contain structural units similar to those of the equi-atomic amorphous alloy with a tetrahedral structure in which each Ge atom is surrounded by four Te atoms, forming $GeTe_{4/2}$ structural units. The introduction of gallium into the stoichiometric $GeTe_4$ matrix leads to variations in the bond angles of the main tetrahedral structural units, and to the appearance of new $Ga_2Te_3$ units with a Ga-Te atomic distance (2.76 Å) [14] larger than the Ge-Te one (2.7 Å) [15] in the $GeTe_{4/2}$ tetrahedral units. The Ga incorporation could modify the entire $GeTe_{4/2}$ structure, distorting it through edge- or corner-sharing linkage of $Ga_2Te_3$ units substituted for the $GeTe_{4/2}$ ones. In $(GeTe_5)_{100-x}Ge_x$, the excess of tellurium atoms with respect to the stoichiometric $GeTe_{4/2}$ matrix determines the existence of homopolar long-distance (2.89 Å) Te-Te bonds [13]. The gallium atoms are more favorably linked to atoms from the tellurium chains, leaving the main tetrahedral units of the glass unaffected. This arrangement with larger distances between the structural units is probably responsible for the observed rearrangement in the structure under higher temperatures, without crystallization of the film.

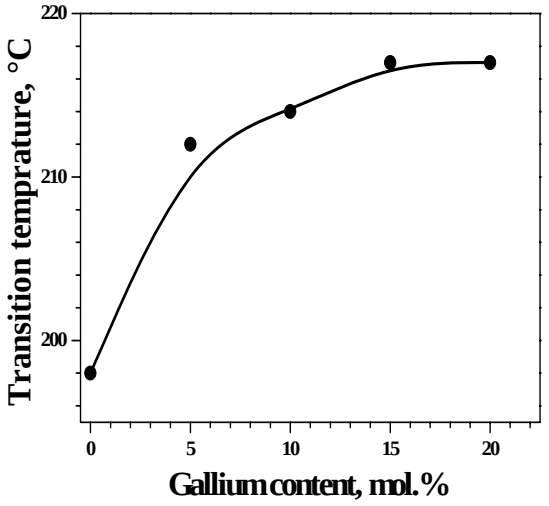


*Fig. 6. Transition temperature vs. Ga content in the $(GeTe_5)_{1-x}Ga_x$ films.*

## 3. Conclusions

Temperature dependent sheet resistance measurements for the alloy with 20% Ga have revealed two transitions at 100 and 250°C, corresponded to structure transformations under higher temperatures,as confirmed by XRD studies. The gradual transition at 90°C possibly indicates relaxation of the amorphous phase, whereas the second rapid transition has been attributed to the amorphous-crystalline transition.

The introduction of gallium modifies the chalcogenide matrix, causing rearrangement in the structure, and leads to an increase in the transition temperature by approximately 20%.

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