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# CRYSTALLIZATION IN CHALCOGENIDE GLASS BY DIFFERENTIAL THERMAL ANALYSIS MEASUREMENTS

E. N. Voronkov

Department of Semiconductor Electronics, Moscow Power Engineering Institute, Krasnokazarmenaja 14, Moscow, 111250, Russia

There are presented the results on a very quick heating of chalcogenide glass up to temperatures slightly higher than its crystallization temperature. The experiments were carried out in specially designed cells for differential thermal analysis. Temperature dependent oscillations have been observed in a narrow range of temperatures and a reasonable discussion of these oscillations is given.

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## 1. Introduction

In chalcogenide glassy semiconductors (CGS) excitation of electron subsystem leads to excitation of structure matrix. The pumped energy stores in generated defects, which have a broad energy spectrum and variety of different behavior. Different defects have different rate of interactions with free charge carriers and different time of relaxation. The ability of defects to interact through free carriers of charge in extended region of defect will enlarge their cooperation.

The self-organization of defects redistributes the stored energy so spatio-temporal behavior of stored energy non-coincides with distribution of supported energy flow. It means that CGS is a nonlinear active medium [1] and the reaction with intensive external excitation depends not only of intensity of excitation, but of the rate of its increase [2, 3].

## 2. Experimental

The aim of the work was to investigate the influence of heating rate on the crystallization process. The Ovshinsky compound - $Ge_{15}Te_{81}As_4$ was used, because it has high crystallization ability. The crystallization was studied by differential thermo analysis (DTA). The special construction of the DTA cells shown in Fig. 1 supported high rate of homogeneous heating of a sample. The DTA cell includes: sensor element and compensating element.

The sensor element was a ball with diameter 0.5 mm, produced from high temperature glass. In this ball the isolated heater and thermocouple were mounted, which were made from very thin wire. The time constant of the element was 0.1 s. This element supported heat rate up to 5000 $^{\circ}$C/s. The reference element had similar construction. The heaters of elements were connected in series. The thermocouples were connected in opposite polarity. Such connection allowed register the temperature difference between the cells.

Before experiments the cell was calibrated and the temperature difference ($\Delta T_0$) between the sensor temperature ($T_s$) and the compensating element temperature ($T_r$) e.g. $\Delta T_0 = T_s - T_r$ was measured in a temperature range. The cells with the minimal temperature difference were used.

In order to deposit a CGS layer, the bulk sample was milled. The particles were separated according their size. The thin fraction with the average size of particles about 1 micrometer was used for experiments. The powder was mixed with ethyl alcohol to make a suspension. The suspension was

deposited by thin and soft brush over the sensor cell ball by a uniform layer. The dried layer was uniform with thickness not more than 20 micrometers.

The amount of a material necessary for performance of measurements did not exceed 0.1 milligram. Small weight of substance, its good contact to a heating up surface, provided small constant time for the CGS film.

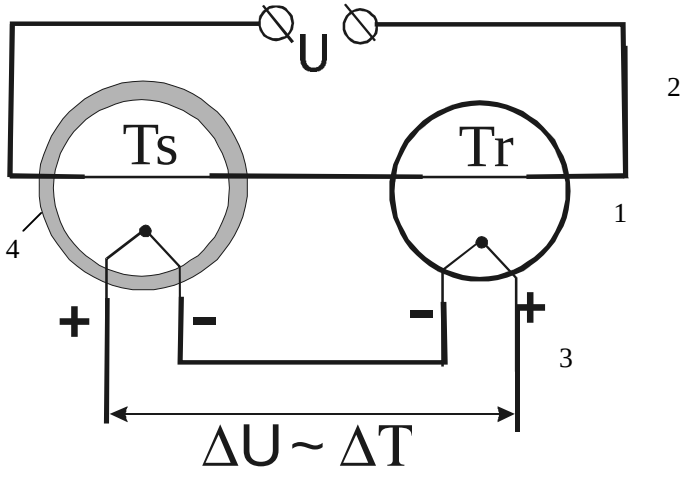


Fig. 1. The arrangement of the DTA cells. 1 – glass balls, 2 - wire heaters, 3 - thermocouples, 4 – a CGS layer.

With the help of the generator of current impulses it was possible to ensure practically any mode of heating. In our experiments two modes were used: i) smooth heating from room temperature up to temperature a little exceeding the temperature of crystallization and ii) fast heating to the temperature and long-run at this temperature. For maintenance of these modes the saw tooth and rectangular current pulses were used accordingly.

In the first case the speed of heating did not exceed 1 $^{o}$C/s, that allowed create almost equilibrium conditions. The DTA diagram for this heating mode is shown in a Fig. 2. The temperature of the sensor cell is drawn in the horizontal axis, while the difference of temperatures between reference and sensor cells is drawn in representative units on the vertical axis.

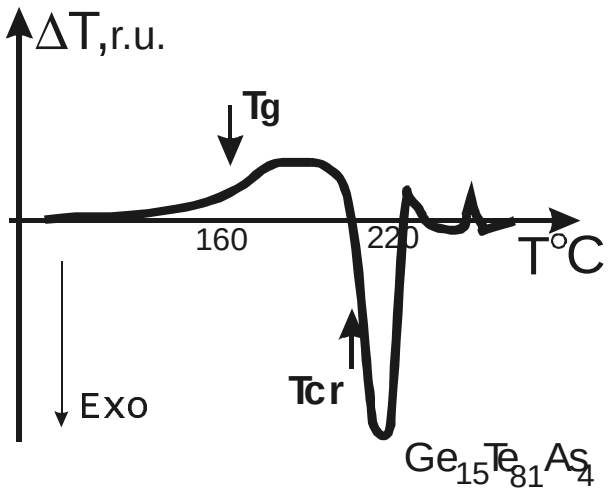


Fig. 2. DTA diagram at low heating rate.

Two areas are clearly visible in Fig. 2: the upper area, which corresponds with an endothermic process in CGS and the lower area, which corresponds to an exothermic process. In area of endothermic process the rate of heating of a sensor cell becomes less than the rate of heating of a compensating cell and a positive difference of temperatures $\Delta T$ establishes between them.

In area of exothermic process the rate of heating of a sensor cell exceeds rate of heating of a compensating cell and $\Delta T$ becomes negative. The occurrence of an endothermic area testifies the beginning of breaking bonds at $T_g$ (glass transition temperature). The exothermic process is related to crystallization.

The subsequent experiments were carried out with a heater which is drived by a rectangular pulse. CGS samples were heated with the greatest possible speed up to the temperature higher than the crystallization temperature ($T_{cr}$) and this temperature was maintained while changes in material occured?

## 3. Results

A result of experiment at step heating is given in Fig. 3. One can see from the recorded diagram, the basic feature of the result consists in the appearance of periodic oscillations, which did not fade during long time and whose disappearance occurs practically instantly. The amplitude of fluctuations could reach 10-20 $^{o}$C. The effect of occurrence of fluctuations at the given mode of heating is well reproduced, though the time of existence of fluctuations could vary from a sample to a sample. At decreasing temperatures the fluctuations became fading. However in all cases their excitation remained rigid, i.e. the fluctuations arose at once with the maximal amplitude. Soft mode, at which an establishment of fluctuations would have the gradual increase of their amplitude in our experiments, was not observed.

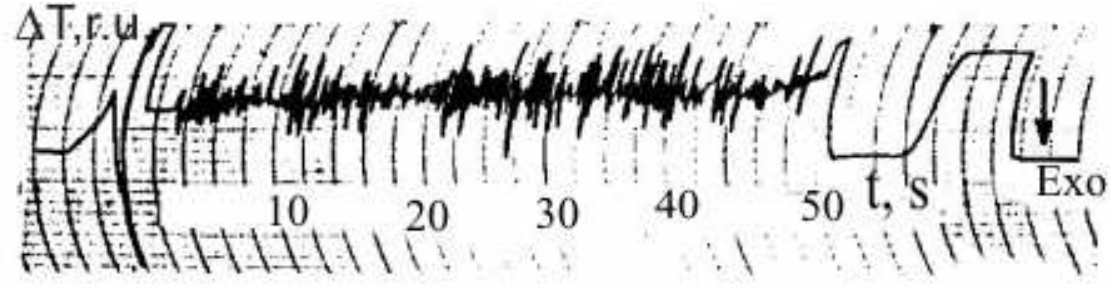


Fig. 3. DTA diagram at step mode of heating.

## 4. Discussion

The registered effect of temperature fluctuations can be considered as a result of non-equilibrium phase transition arising near the temperature of crystallization.

The non-equilibrium transition results from fast heating, which became possible in the designed cells, because practically instant transition of a material took place to an overheated state above at once of two characteristic temperatures - the glass transition temperature $T_g$ - the temperature of softening and the crystallization temperature $T_{cr}$. Those temperatures characterize the beginning of two competing processes - one with break of bonds and absorption of energy, another with formation of bonds and release of heat. The system appears in an unstable transitive condition, the transition from which takes place to a stationary oscillatory state. This dynamic state corresponds to non-uniform system in which separate areas are glassy, and others are polycrystalline. Between these areas and the heater there is a good thermal contact. The result is the periodically repeated cycle either exo- or endothermic process, as it is shown by registering the temperature change. According to the area of the DTA curve the fluctuations cover 15 - 20 % from all volume of CGS.

The long time coexistence of two processes: melting and crystallization is possible only in the case of equal rates of generation and breaking of bonds. This is possible only in a narrow range of temperatures, as proved experimentally. The temperature, for which the fluctuations were observed, did not exceed 40 $^{o}$C. The occurrence of fluctuations is preceded by a delay, that typically corresponds to a nonequilibrium phase transition. Fig. 3 shows, that during the delay period, exo- and endothermic processes took place. The complete disappearance of fluctuations is preceded by long enough period including both exo- and endothermic states, i.e. transition of system in a new condition is preceded by some delay.

The considered effect in many respects looks like the transition to developed turbulence and we believe it can be described by a stochastic model [2].

## 5. Conclusion

The experiments have shown, that an intensive heating of CGS results in a nonlinear oscillation process similar to the case of electrical or acoustic excitation [3, 4].

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