

THE INFLUENCE OF HYDROSTATIC PRESSURE ON THE ELECTRIC CONDUCTIVITY OF AMORPHOUS SEMICONDUCTOR $As_{14}Tl_4Sb_6Se_6Te_{21}$

JOZEF ZÁMEČNÍK*, IVAN BANÍK*, EVA SKOČKOVÁ*,
JURAJ DOUPOVEC**, Bratislava

This paper presents the experimental results obtained on the amorphous semiconducting glass $As_{14}Tl_4Sb_6Se_6Te_{21}$, under hydrostatic pressure up to 6 kbar. The above mentioned material shows switch and memory effects. It is shown that the V_A characteristics of amorphous semiconductors are substantially changed by hydrostatic pressure. Due to experimental results it is suggested to express the V_A characteristics as the function of pressure. It is assumed that the change of the electrical conductivity is caused by the change of the activation energy, the value of which is $\delta E_0 = 0.38$ eV at atmospheric pressure. The measurements show that the change of the activation energy does not depend on the pressure linearly, but $(\partial(\delta E)/\partial p) \approx -1.5 \times 10^{-6}$ eV bar $^{-1}$, in the pressure range of 0–1 kbar. The assumption of the pressure dependence of the activation energy was proved also by measurements of the pressure dependence and temperature dependence of the electrical conductivity.

I. INTRODUCTION

The theory of amorphous materials, including semiconductors, has not been worked out satisfactorily yet. The complicated structure of these materials makes their theoretical analysis very difficult. Therefore at present the attention is mainly concentrated on collecting experimental material and the knowledge obtained can be the starting point for making a unified theory of amorphous materials.

The present state of the band structure theory of disordered systems is represented by the *CFO* model (Cohen, Fritzsche, Ovshinsky), [1–3] for an ideal semiconducting glass, completed by Böer [4] for the real glass. Taking $E = \frac{1}{2}(E_c - E_v)$ as the activation energy, where E_c and E_v are according

* Katedra fyziky Elektrotechnickej fakulty SVŠT, Gotwaldovo nám. 2, 880 19 BRATISLAVA, Czechoslovakia.

** Fyzikálny ústav SAV, Dohrávská cesta, 899 30 BRATISLAVA, Czechoslovakia.

to [1] the edges of mobility in the valence band respectively, then the activation energy in an amorphous semiconductor is according to [4] by about 0.25 eV greater than in the same crystalline material. This fact, as well as some other common properties of disordered systems are explained in [5, 6].

One of the important factors used for studying the energy structures of semiconductors is the mechanical pressure. It is known that the spectrum of electrons in matter is determined by the interatomic dimensions. Mechanical pressure changes their dimensions and therefore influences directly also the energy spectrum. Studying the pressure dependence of the electrical properties of semiconductors contributed to a detailed understanding of the band structure as well as of the transport properties of crystalline materials [7]. From that point of view it seems to be interesting to apply the high pressure technique also to the broad range of amorphous solids having low mobility. It can be expected that by means of the effects caused by pressure it may be possible to obtain important material constants also for amorphous semiconductors.

II. EXPERIMENTS

In this paper there are given the experimental results obtained on the bulk samples of the chalcogenide glass of the composition $As_{14}Tl_{14}Sb_8Se_{16}Te_{24}$. All raw materials used in the preparation of the glass were of high initial purity (99.999%). The elements were weighed with a high accuracy loaded into a fused silica ampoule. The total diameter of the ampoule was $\varnothing \sim 10$ mm and the total of the elements was ~ 10 g. The ampoule was evacuated to a pressure of less than 2×10^{-5} torr 6 hours before sealing off and gradually heated up to 950 °C. The ampoule was stirred and turned during the heating because of the acceleration of the synthesis and homogenization of hot metals at this temperature. Then it was cooled only by the spontaneous cooling in air, at room temperature. The silica ampoule was removed by dissolving in hydrofluoric acid. The required shape of the measured samples was obtained by means of cutting, grinding and polishing. The relatively high specific resistance ($\sim 10^5 \Omega \text{cm}$), as well as a glassy appearance, were the characteristic features of these samples. The lack of characteristic crystalline diffraction patterns at the rtg. diffraction (Debye-Scherrer camera, $\text{CuK}\alpha$ reflected radiation) proved the amorphous structure of these samples.

The basic characteristics of this amorphous material were obtained by means of the differential thermal analysis (DTA). In Fig. 1 a typical DTA thermogram is given. The sample was heated at the rate of 20 °C/min and pure alumina was applied as a reference material. According to the measurement there is a glass transition temperature $T_g \approx 105$ °C. It is possible

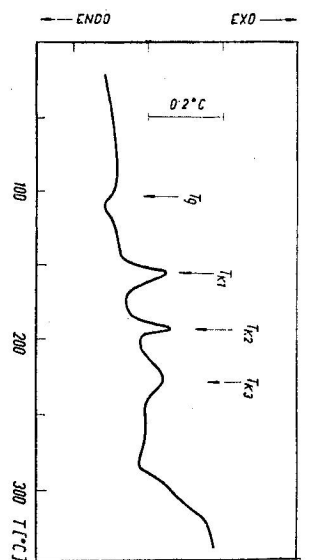


Fig. 1. DTA of chalcogenide glass. Temperature rate 20 °C/min, sample weight 6.9 mg, ambient atmosphere — air, reference material — Al.

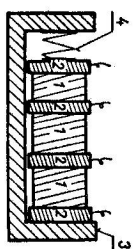


Fig. 2. Diagram of the sample in the holder. 1 — the sample, 2 — contact, 3 — holder, 4 — spring.

to assume at the existence of the characteristic dependence near the glass transition in the DTA thermogram (according to the 2/3 law [8]) and the rtg. diffraction analysis is sufficient evidence of the amorphous state of our material.

All pressure influenced measurements were taken in the static regime at DC fields under $4 \times 10^2 \text{ V cm}^{-2}$. A good ohmic contact was produced by covering the copper aerial contacts by gallium. Fig. 2 illustrates the arrangement of samples in the holder. VA characteristics were drawn by a type ENDIM 2200 XY recorder, (precision range 0.4%). The temperature in the vicinity of the samples was measured by a Cu-Ko thermocouple with an error of ± 0.2 °C. As shown later the relative change of the activation energy was established from the measured VA characteristics. To check these results a temperature dependence of electrical conductivity was measured by the Van der Pauwe method [9] under atmospheric pressure and the pressure conductivity was measured in the temperature range of $19 \text{ °C} < T < 100 \text{ °C}$. The pressure was applied to the sample by means of pressure oil. A set of six samples of various thickness obtained from one melting process was pressed in the device described in [10] arranged for temperature measurements.

III. RESULTS

The results obtained in all samples are quantitatively identical. VA characteristics measured at a pressure of 0—6 kbar are illustrated in Fig. 3.

The VA characteristic at an atmospheric pressure for the sample in the

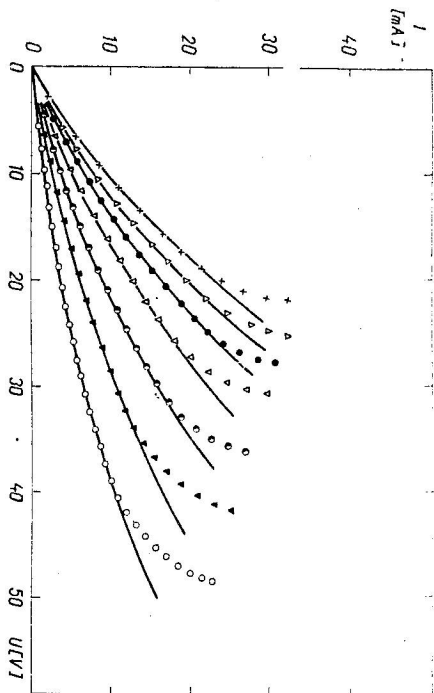


Fig. 3. I - A characteristics of the chalcogenide glass $As_{14}Ti_{14}Sb_6Se_6Te_1$ depending on the hydrostatic pressure. \circ — atmospheric pressure, \blacktriangledown — 1 kbar, \bullet — 2 kbars, ∇ — 3 kbars, \bullet — 4 kbars, \triangle — 5 kbars, $+$ — 6 kbars, — calculated from the relation (10).

OFF state can be according to [11] approximated very well by the expression

$$I = AU \exp bU \quad (1)$$

where A and b are material parameters, I is the intensity of the electric current passing through the sample and U is the voltage between contacts. We have found that the characteristics at various pressures can be also expressed by relation (1), but A and b are parameters now depending on pressure.

Pressure caused changes of I - A characteristics can be explained by the fact that hydrostatic pressure changes the activation energy of a given material [12—14]. The change of activation energy in the range of small electric fields can be under that assumption estimated from the measured characteristics [14] according to the relation

$$\Delta E = \delta E_0 - \delta E = kT \ln \frac{R_0}{R} \quad (2)$$

where δE_0 is the activation energy and R_0 the sample resistance at 0 bar, δE is the activation energy and R the sample resistance at the pressure p , k is the Boltzmann constant, T the sample temperature. The values R and R_0 can be found from the slope of the linear part of the curves illustrated in Fig. 3. The dependence $\Delta E = f(p)$ determined from the measured characteristics by means of the expression (2) is illustrated in Fig. 4. Measurements show

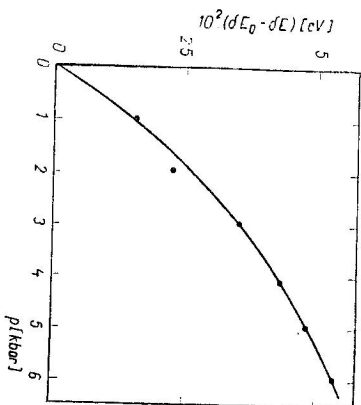


Fig. 4. The change of activation energy in dependence on the hydrostatic pressure.

that in the pressure range of 0—1 kbar we have $(\partial(\delta E)/\partial p)_T = \lim_{I \rightarrow 0} (\Delta E/\Delta p)_T \approx 1.5 \times 10^{-5}$ eV bar $^{-1}$, which is in relatively good agreement with the value obtained from the dependence $\ln \sigma(1/T)$, illustrated for two various pressures in Fig. 5. Experimental data show that the dependence of $\ln \sigma$ on $1/T$ is practically linear. According to [15] measurements of the temperature dependence of electric conductivity at $As_2(Se, Te)_3$ glass does not give a linear function for $\delta E(T)$, but there must be also an expression with the square of the temperature. Having approximated the $\ln \sigma = f(1/T)$ dependence by linear dependence, then the activation energy of the investigated glass at atmospheric pressure equals $\delta E_0 = 0.38$ eV. For the pressure range of 0—1 kbar we have

$$\left(\frac{\partial(\delta E)}{\partial p} \right) \approx -1.5 \times 10^{-5} \text{ eV bar}^{-1}.$$

These results prove the fact that the activation energy is changed by hydrostatic pressure. As the pressure change of mobility is not measurable, [16], then the pressure influences the concentration of charge carriers by means of a change of the activation energy and so it essentially influences electrical conductivity [17].

The pressure dependence of electrical conductivity is primarily caused by the pressure influence on the injecting properties of contact according to [16], where the results obtained in amorphous selenium are presented. Although the influence of contacts cannot be completely excluded, we supposed that fact not to be decisive at a hydrostatic pressure.

It is shown (Fig. 4) that under higher pressure the change of the activation energy ΔE is no more a linear function of pressure. In the pressure range,

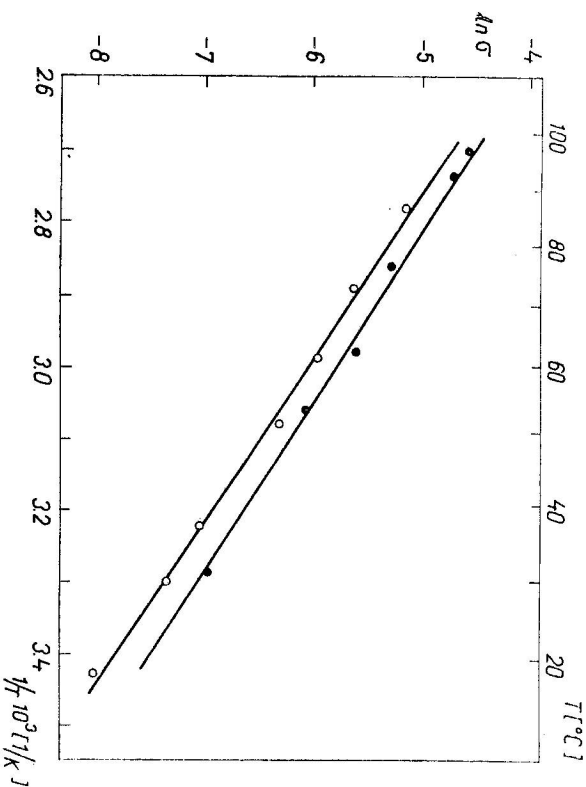


Fig. 5. Temperature dependence of electric conductivity. Δ — atmospheric pressure, \blacksquare — 1 kbar.

where measurements were performed, it can be approximated well by the function

$$\Delta E(p) = C_1 p + C_2 p^2 \quad (3)$$

where C_1 and C_2 are the characteristic constants of the material at a given temperature.

The electrical conductivity σ of amorphous semiconductors can be generally explained by the expression

$$\sigma = \sigma^* \exp \left[-\frac{\delta E}{kT} \right] \quad (4)$$

where δE is the activation energy, k the Boltzmann constant, and T the sample temperature, which changes in the sample due to the Joule heating. The preexponential factor σ^* is about $10^3 \Omega^{-1} \text{cm}^{-1}$. On the basis of expression (4), the electrical conductivity of amorphous semiconductors can be written in the form

$$\sigma = \sigma^* \exp \left[\frac{\Delta E}{kT} \right] \quad (5)$$

The expression (3) and (5) yield the pressure dependence of electrical conductivity

$$\sigma = \sigma_0 \exp [\alpha p + \beta p^2], \quad (6)$$

where σ_0 is the electrical conductivity at the pressure of $p = 0$, $\alpha = C_1/kT$, $\beta = C_2/kT$. In the range of small electric fields there is in the expression (1) $e^{bV} \approx 1$, hence $I = AU$, where A is the reciprocal value of resistance,

$$A = \frac{1}{R_0} \exp [\alpha p + \beta p^2], \quad (7)$$

where R_0 is the resistance at the pressure $p = 0$.

By using the expression (7), the current intensity can be written

$$I = \frac{U}{R_0} \exp [\alpha p + \beta p^2]. \quad (8)$$

Therefore the relation (8) expresses the VA characteristics in their linear region. Due to the above mentioned reason, relation (8) is not valid at higher electric fields. In that case it is necessary to use the more common relation (1) and to take into consideration the fact that not only the parameter A , but also the parameter b are functions of pressure. The values of parameter b for various pressures can be estimated from the slope of the linear part of the $\ln I = \ln AU + bU$ type dependences illustrated in Fig. 6. From the measurements it results that the pressure dependence of parameter b can be approximated by the relation

$$b = \gamma + \delta p + \omega p^2, \quad (9)$$

where γ , δ , ω are characteristic material constants. By means of (7) and (9), from the relation (1) we can express the VA characteristic in the form

$$I = \frac{U}{R_0} \exp [\alpha p + \beta p^2 + U(\gamma + \delta p + \omega p^2)]. \quad (10)$$

Putting in the relation (10) $p = 0$, and taking into consideration the dependence (7), we reach the expression (1).

Figure 3 illustrates the comparison of measured VA characteristics with the curves given by the relation (10) for the values of constants: $R_0 = 8.33 \times 10^{-3} \Omega$, $\alpha = 0.549 \text{ kbar}^{-1}$, $\beta = -4.23 \times 10^{-2} \text{ kbar}^{-2}$, $\gamma = 1.90 \times 10^{-2} \text{ V}^{-1}$, $\delta = -0.170 \times 10^{-2} \text{ kbar}^{-1}$, $\omega = 3.65 \times 10^{-4} \text{ kbar}^{-2}$.

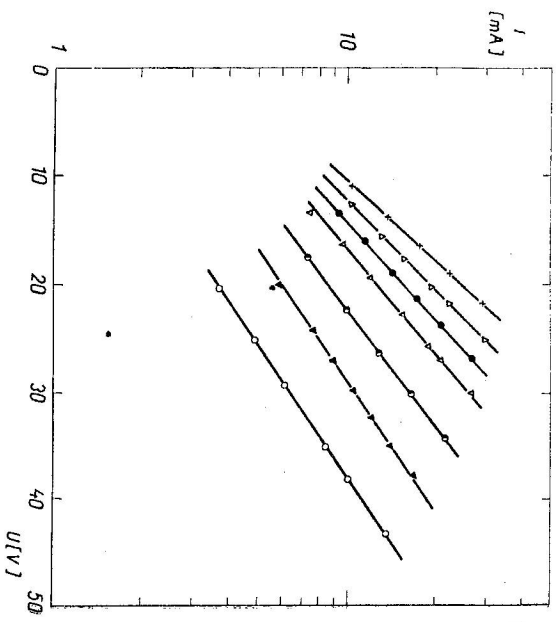


Fig. 6. $V-I$ characteristic depending on the hydrostatic pressure in a semilogarithmic scale.

A relatively good correlation can be seen in the applied pressure range. More evident deviations do not occur till near the critical voltage, when the sample begins to switch to the ON state. Not even the basic expression, however, covers that range.

The switching mechanism has not been satisfactorily explained yet. In the case of thick samples, (over 10 μm), the switching effect is according to [18] caused by the thermal breakdown due to the Joule heating.

In the case of the current impulse caused by a break, discussed in paper [18] for a voltage linearly increasing in time U_{in} , we get the expression

$$U_{in} \sim [k^2 T_0^2 / \sigma(T_0)]^{1/2}, \quad (11)$$

where h is the sample thickness, that means the distance of the area contacts and T_0 is the ambient temperature. Using the expressions (6) and (11) for the constant ambient temperature, we find that the switching voltage U_{in} decreases with pressure approximately as $U_{in} \sim \sigma^{-1/2}$, which agrees with the measured values illustrated in Fig. 7. Similarly in agreement with relation (11) we reach the dependence of the switching voltage on the sample thickness. The measured values of the switching voltage on samples of various thickness under various hydrostatic pressures are illustrated in Fig. 8.

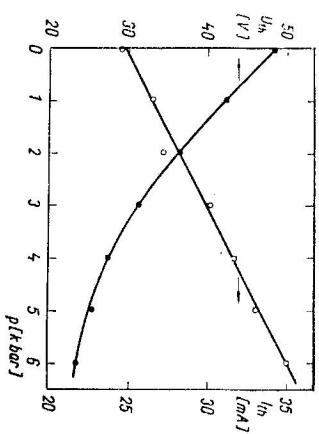


Fig. 7. Dependence of the switching voltage U_{in} and the switching current on the hydrostatic pressure.

IV. CONCLUSION

It is shown, as it was expected, that in the case of the more component semiconductive chalcogenide glass the hydrostatic pressure changes substantially the electrical conductivity. This fact can be explained by the assumption of a change of the activation energy of the material under the hydrostatic pressure. The bending of the $V-I$ characteristic and the beginning of the switching into the ON state are probably caused by a temperature increase in the sample due to the Joule heating. However, a proper switching and the state after the switching have an evidently electronic behaviour because

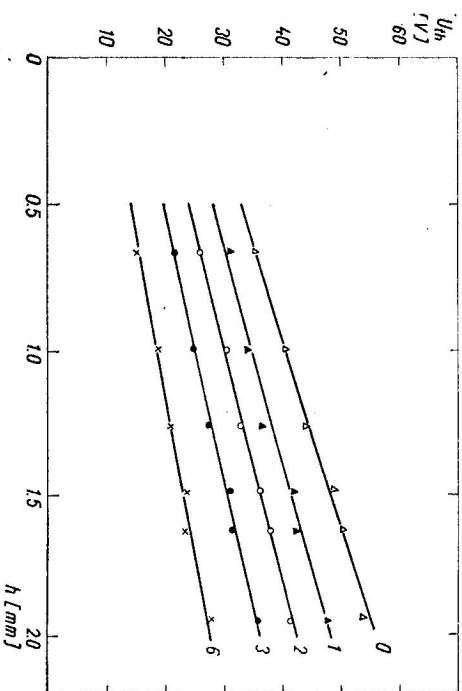


Fig. 8. Dependence of the switching voltage U_{in} on the sample thickness h . Δ — atmospheric pressure, \blacksquare — 1 kbar, \square — 2 kbars, \bullet — 3 kbars, $+$ — 6 kbars.

our investigation agrees with the results discussed in papers [19, 20]. As the switching voltage is decreasing with pressure, it can be expected that the sample can also be switched into the ON state only by pressure.

ACKNOWLEDGEMENTS

The authors are very grateful to DrSc. J. Krempaský for valuable remarks and suggestions.

REFERENCES

- [1] Cohen M. H., *X Internat. Conf. Phys. Semicond.*, Cambridge, Mass. 1970; *J. Non-Cryst. Sol.*, **4** (1970), 391; *Physics Today* **24** (1971), 26.
- [2] Mott N. F., *Festkörper Probleme*, **9** (1969), 22; *Phil. Mag.*, **22** (1970), 1.
- [3] Cohen M. H., Fritzsche H., Ovshinsky S. R., *Phys. Rev. Lett.*, **22** (1969), 1065.
- [4] Böer K. M., *Phys. Stat. Sol.* (a), **3** (1970), 1007.
- [5] Krempaský J., *Melzindr. konf. o amorf. polov.*, Soňa 1972.
- [6] Krempaský J., Dieška P., *Phys. Stat. Sol.*, (b) **56** (1973), 365.
- [7] Paul W., Warschauer D. M., *Solids Under Pressure*, Mc GRAW-HILL BOOK Company, Inc., New York, San Francisco, Toronto, London, 1963.
- [8] Sakka S., Mackenzie J. D., *J. Non-Cryst. Sol.*, **6** (1971), 145.
- [9] Macko P., *Praktikum z fyziky polovodičov*, SVŠT, Bratislava 1970.
- [10] Zámečník J., Baník I., Zatkovič J., *Čs. Čas. fys.*, **A 22** (1972), 465.
- [11] Krempaský J., Červenák J., Dieška P., Kubek J., *Phys. Stat. Sol.*, **6** (1971), 415.
- [12] Fagen E. A., Holmberg S. H., Seguin R. W., Thompson J. C., Fritzsche H., *X Intern. Conf. Phys. Semicond.*, Cambridge, 1970.
- [13] Koroľmenč B. T., Pachonova E. M., *Физ. техн. полупров.*, **6** (1972) 1403.
- [14] Zámečník J., *Czech. J. Phys.*, **B 21** (1971), 1302.
- [15] Roilos M., Meimaris D., Zigris K., *J. Non-Cryst. Sol.*, **7** (1972), 271.
- [16] Doležal E. K., Spear W. E., *J. Non-Cryst. Sol.*, **4** (1970), 97.
- [17] Baník I., Zámečník J., *Czech. J. Phys.*, **B 23** (1973), 479.
- [18] Fritzsche H., Ovshinsky S. R., *J. Non-Cryst. Sol.*, **4** (1970), 464.
- [19] Barančok D., Dieška P., Krempaský J., *Phys. Stat. Sol.* (a), **16** (1973), 253
- [20] Krempaský J., *private communication*.

Received May 8th, 1973