acta phys. slov. 27. (1977), No. 3

EVIDENCE FOR TWO GROUPS OF DEEP LOCAL LEVELS IN THE ENERGY SPECTRUM OF Al-DOPED GLASSY As_2Se_3 BY THERMAL DIELECTRIC RELAXATION

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Two overlapping peaks are resolved in the dielectric relaxation current (DRC) spectrum of Al-doped glassy As_2Se_3 for Al content greater than 0.1 at %, whereas only the 300 K (0.84 eV) peak present also in pure As_2Se_3 glass could be detected for lower Al concentrations. The latter peak can be almost completely annealed out by thermal treatment and is thus attributed to a spectrum of metastable deep recombination centres like holes localized on the chalcogen, the centres lying near the middle of the gap. Introduction of greater amounts of Al leads to the appearance of an additional DRC peak at about 280 K (0.78 eV), which is tentatively ascribed to broken Al–Se bonds (partly ionic), the Al^+ center acting as acceptor.

Direct determination of trap parameters is complicated by several circumstances, the complexities involved in DRC analysis being discussed.

ДОКАЗАТЕЛЬСТВО ДВУХ ГРУПП ГЛУБОКИХ ЛОКАЛЬНЫХ УРОВНЕЙ В ЭНЕРГЕТИЧЕСКОМ СПЕКТРЕ СТЕКЛООБРАЗНОГО СОЕДИНЕНИЯ As_2Se_3 С ПРИМЕСЬЮ АЛЮМИНИЯ НА ОСНОВЕ ТЕРМИЧЕСКОЙ ДИЭЛЕКТРИЧЕСКОЙ РЕЛАКСАЦИИ

Б спектре тока диэлектрической релаксации стеклообразного соединения As_2Se_3 с примесью алюминия обнаружены два перекрывающихся пика при содержании алюминия свыше 0,1 ат. % в то время как для низших концентраций алюминия может быть обнаружен только один пик при температуре 300 K (0,84 эв), который присутствует также в чистом стекле As_2Se_3. Последний пик может быть почти полностью снят с помощью термической обработки и таким образом относится к спектру метастабильных глубоких центров рекомбинации подобных дыркам, локализованным на халькогене, которые лежат вблизи от середины запрещённой зоны. Введение больших количеств алюминия приводит к появлению добавочного пика в токе диэлектрической релаксации при температуре около 280 K (0,78 эв), который в предварительном порядке приписан нарушению связей Al–Se (частично ионных), причём центр Al^+ действует как акцептор.

Прямое определение параметров ловушек сложно по нескольким причинам. Сложности анализа тока диэлектрической релаксации, обсуждаются в статье.

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I. INTRODUCTION

Kolomiets and his coworkers [1, 2] were among the first who investigated the influence of impurities upon the energy spectrum of deep recombination centres in glassy As_2Se_3. An exhaustive review of the work concerning the role of impurities in chalcogenide glasses was presented by Kolomiets [3]. The fact that the glasses are insensitive to doping has often been attributed to a high concentration of intrinsic defects [4], as well as to the possibility of satisfying almost all covalent bonds of impurity atoms in a disordered glass matrix [5].

Little attention, to our knowledge, has been paid to the physical properties of chalcogenide glasses doped with aluminium [6]. Only a few data on the frequency and temperature dependence of the real part of the dielectric constant and of ac conductivity of glassy As_2Se_3 doped with elements of the III A group were published [7].

The present paper deals mainly with the character of changes observed in the energy spectrum of deep localized states of glassy As_2Se_3 doped with Al up to 1.5 at %. Throughout the paper the results obtained are discussed in terms of the theory of thermal dielectric relaxation, formulated first by Simmons and Taylor [8, 9] for metal–insulator–metal (M–I–M) systems and adopted elsewhere for the interpretation of dielectric relaxation in pure glassy As_2Se_3 [10] in the sense of energy levels around the Fermi level. Moreover, it has been suggested that there is a distribution of energy levels rather than a discrete peak near the Fermi level in the As_2Se_3 glass [11]. Recently, Müller has questioned such interpretation of thermal dielectric relaxation in the bulk As_2Se_3 glass [12], so that further arguments will be presented which support the interpretation of thermal dielectric relaxation [10, 11] in terms of local levels for majority carriers.

II. EXPERIMENTAL PROCEDURE

II. 1. Sample preparation

The samples of $As_2Se_3 + x$ at % Al were prepared by adding defined quantities of elemental metallic aluminium to purified vitreous As_2Se_3 [13]. All the samples were prepared under identical temperature regime, the synthesis being performed at 1173 K during 8 hours. The melt was cooled by placing the crucible into an oven held at 523 K for 3 hours, this was followed by spontaneous cooling of the oven down to room temperature.

II. 2. Experimental procedure

The measurements were started 48 hours after the evaporation of Al contacts had been accomplished. In order to bring the system Al—As_2Se_3—Al into the steady state, a voltage V_d was applied to the system at a temperature $T_p \geqslant 310$ K for a time t_p with subsequent cooling under the applied voltage to ~ 200 K, at which temperature the system was shortcircuited by a resistor $10^9\ \Omega$. The thermal dielectric relaxation current was registered by an electrometer VIBRON 33C when heating the system at a constant heating rate of 0.17 Ks^{-1}.

III. RESULTS AND DISCUSSION

III. 1. DRC in pure As_2Se_3 glass

The changes in the dielectric relaxation current (DRC) spectrum $I - T$, observed if x at % of Al are introduced into pure As_2Se_3 glass, are evident from an inspection of Fig. 1. If the Al content has not exceeded about 0.1 at %, which corresponds to the concentration of 10^{20} cm^{-3}, only the 300 K peak present also in pure glassy As_2Se_3 is observed [10, 11]. The behaviour of the latter with respect to the magnitude of the voltage applied [14] is such that the small signal capacitance $C_\lambda = \Delta Q/\Delta V$, where Q denotes the charge accumulated in the depletion region, is an increasing function of V_d. This is an unusual situation when compared with that of the Schottky-barrier to crystalline semiconductors involving one discrete trapping level [8, 9]. Another surprising feature of the 300 K peak, observed in the Al—As_2Se_3—Al system not thermally treated prior to measurements, is illustrated in Fig. 2. On repeating the measuring cycle the 300 K peak height is successively reduced, whereas the 320 K peak¹) is not affected by thermal treatment. Thus it is evident that the change in the intensity of the former peak is not due to thermally induced changes in the barrier height. This important statement will be confirmed in an independent way in connection with the analysis of DRC in Al-doped glassy As_2Se_3. Moreover, annealing the system for several hours at 390 K reduced the 300 K peak to such an extent that it was purely resolved only at the low temperature tail of the 320 K peak. Since during the preparation of the Al contacts the samples were illuminated by visible light, one should check the possibility of relating the occurrence of the 300 K to photoinduced changes in the material. As proved experimentally, the 300 K peak height was considerably restored by illuminating the annealed sample and providing it with new electrodes, which fact seems to confirm our hypothesis of a connection between photoinduced structural changes and the 300 K peak of DRC.

Recently, Bishop, Strom and Taylor revealed irradiation-induced mid-gap absorption in both As_2Se_3 and As_2S_3 glasses [15, 16] at low temperatures, accompanied by an observation of an electron spin resonance (ESR). These

¹) The 320 K peak might be due to a quasi-steady-state to equilibrium relaxation, free charge polarization etc.

optically induced paramagnetic states are now believed to be responsible for the observed fatiguing of the photoluminiscence efficiency during continuous excitation [17, 18]. Following the model of the gap states developed by Mott, Davis and Street [19], photogenerated electrones and holes are rapidly captured by D^+ and D^- centres, forming in both cases singly occupied neutral D centres. Due to the

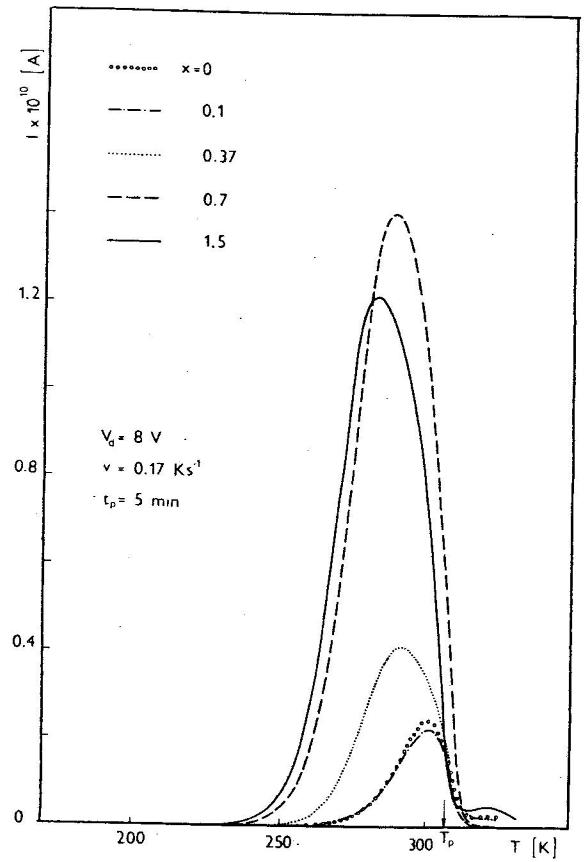


Fig. 1. DRC in Al—As_2Se_3: x at % Al—Al system.

relaxation of the lattice these D centres lie near the middle of the gap [20]. Then the induced mid-gap absorption represents reexcitation of the holes localized on chalcogen atoms [15].

We suggest that the deep gap states which give rise to the 300 K peak are the metastable D states. Their residual concentration near room temperature should be

much lower than 10^{15} cm^{-3}, since no ESR signal in glassy As_2Se_3 could be detected at this temperature [21]. An exact calculation of the density of the states meets with serious difficulties connected mainly with the superlinear dependence of DRC upon V_d [14]. Starting from measurements of an optically induced absorption [15], one would expect a distribution of energy levels rather than a sharp maximum of a density of states in the middle of the gap. Thus, we try to explain the unusual $Q(V_d)$ dependence of the 300 K DRC peak as due to the filling of a spectrum of traps about the Fermi level. Unfortunately, no rigorous treatment of this case is available at present. Later a rough estimate will be obtained of the residual concentration of filled traps N_t, which might be consistent with the failure to obtain evidence for these traps by other techniques at elevated temperatures.

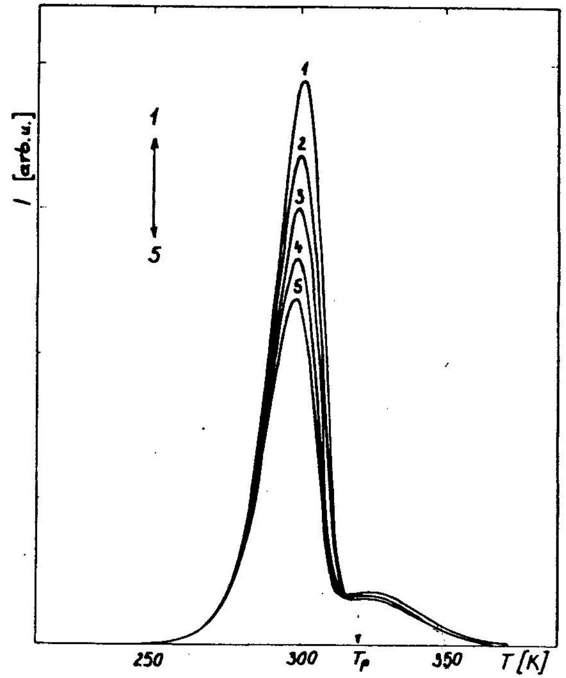
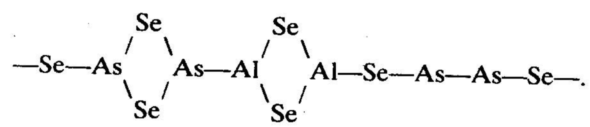


Fig. 2. DRC in Al—As_2Se_3—Al, the numbers indicating the sequence of individual thermal cycles.

In spite of the difficulties associated with the determination of the trap density, we can definitely state that the charge flowing in the system during relaxation does not represent the detrapping of injected excess minority carrier. Calculating the total observed charge Q from the curve $x = 0$ in Fig. 1, one finds the equivalent capacitance $C_e = Q/V_d$ to be about one order of magnitude greater than twice the geometrical capacitance C_u. As it is well known, the capacitance of a capacitor with an injected space charge cannot exceed $2C_u$ [22], so that charge injection might be excluded from further considerations as expected also with regard to the voltage/thickness ratio of 10^2 V/cm. Then the observed relaxation phenomena are most probably related to the formation of a depletion region at the interface metal-semiconductor [8, 9].

III. 2. DRC in Al-doped As_2Se_3 glass

Now let us turn our attention to the changes in the DRC spectrum associated with the introduction of Al into glassy As_2Se_3. As indicated in Fig. 1, if up to 0.1 at % Al is introduced, no significant changes in the DRC are observed in comparison with the undoped material. Only the 300 K peak is present again at temperatures above 200 K and its magnitude is considerably reduced after thermal cycling (Fig. 3), as expected. The length of polymeric chains is probably little affected by doping, the Al impurity occupying some sites of As:



The suggested structural chain follows from the expected reaction between the basic material and the dopant during melting

$$As_2Se_3 + x\,Al \rightarrow \left(1-\frac{3x}{2}\right) As_2Se_3 + \frac{x}{2} Al_2Se_3 + \frac{3x}{2} As_2Se_2.$$

In contrast, the introduction of aluminium in amounts greater than 0.1 at % caused remarkable changes in DRC spectrum (Fig. 1). Both shape and halfwidth of the thermograms altered, the latter increased from 20 K in pure As_2Se_3 to 33 K in glasses containing 0.7 and 1.5 at % Al, respectively. The DRC of glassy As_2Se_3 doped with 0.7 at % Al was analysed in more detail. As pointed out by Simmons and Taylor [9], if more than one trapping level is operative, the DRC spectrum will consist of several peaks. We have adopted the hypothesis that the DRC of glassy As_2Se_3 with more than 0.1 at % Al might be composed of two peaks, one of them being the 300 K peak of the pure material. To check the correctness of this conception, one had first to show both maxima to result from bulk-determined relaxation from steady-state to quasi-steady-state [9]. As evident from Fig. 4, where the upper $I-T$ characteristic corresponds to the upper electrode biased positively, an almost completely symmetrical characteristic is obtained after a bias

polarity reversal (bottom curve). Thus we have concluded that the total $I-T$ characteristic results from a bulk-limited dielectric relaxation and not from a quasi-steady-state to equilibrium relaxation, the latter being an electrode-limited process [9].

The resolution of individual peaks in DRC from Fig. 4 is far from straightforward. Further a procedure of decomposition we have intuitively anticipated as

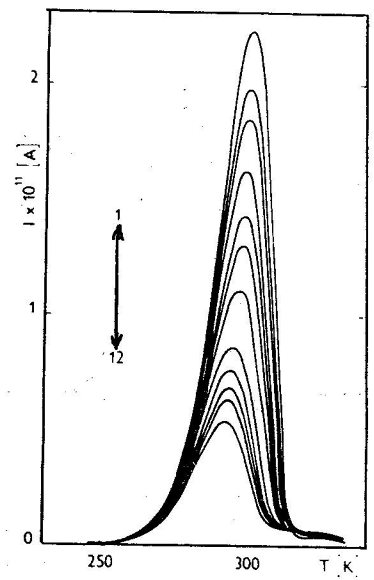


Fig. 3. DRC in Al—As_2Se_3—Al system observed when repeating thermal cycles, $T_p = 410$ K, $t_p = 5$ min.

a correct one will be shown. The system metal-semiconductor-metal was biased at $T_p = 260$ K for various times t_p, the respective thermograms are shown in Fig. 5. The maximum temperature T_m ceased to move if the system was biased for $2\,\text{min} < t_p < 15$ min., for longer time intervals T_m shifted to higher temperatures again as a consequence of the growth of the high temperature tail of the total spectrum. We hope that the reader will agree with our suggestion to regard the curve d from Fig. 5 as a distinct peak with T_m located at ~ 280 K. The activation energy of the latter was estimated to be 0.78 ± 0.02 eV from the initial rise. After subtracting the 280 K peak from the total DRC it becomes evident that the 300 K peak is present in heavily doped a-As_2Se_3, too (Fig. 6).

Our last conclusion is supported also by the observation of a systematic reduction of the high temperature portion of the total DRC on thermal cycling, illustrated by Fig. 7. In addition, in Fig. 7 further evidence is presented that the decrease in size of the 300 K peak is not primarily due to changes in the contact barrier height, othervise reduction of the complete spectrum should be observed.

Applying bias voltages between 1 and 10 V under the conditions corresponding to the curve d from Fig. 5, the set of thermograms in Fig. 8 was obtained. It is worthy to note that a slight shift of T_m towards lower temperatures with an increasing bias could be detected in agreement with the prediction made by Gupta

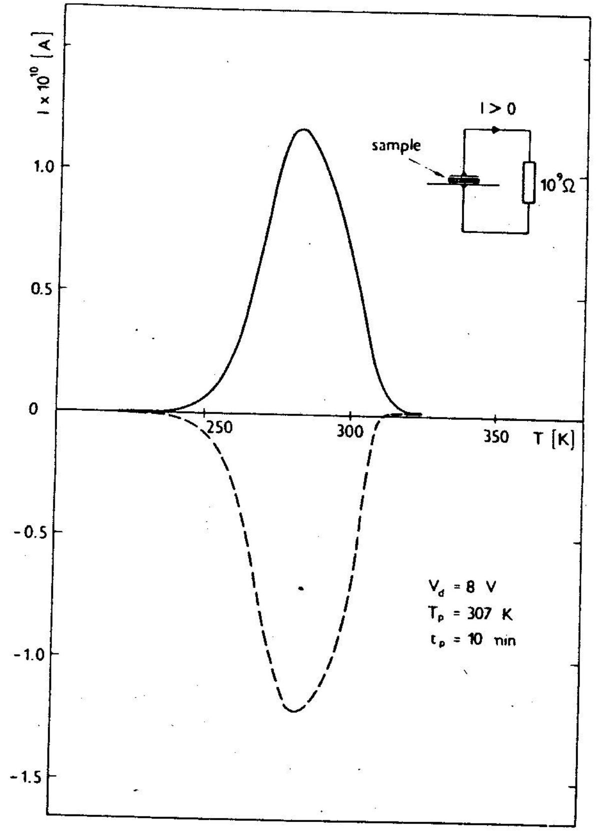


Fig. 4. The upper thermogram (full line) was obtained with the top electrode charged positively, the dashed line with bias reversed — Al—As_2Se_3: 0.7 at % Al—Al.

and van Overstraeten [23] concerning DRC resulting from one discrete trapping level. Thus, we have concluded that a quasi-discrete trapping level is introduced by the addition of Al in amounts greater than 0.1 at %.

The nature of the additional trapping center associated with Al doping, which manifests itself as the 280 K DRC peak, cannot be definitely established as long as

no further data on the same subject are available. Therefore, we will restrict ourselves solely to a tentative explanation, which is based on the following experimental findings:

1. In heavily doped As_2Se_3 glass the magnitude of the 300 K peak seems to be considerably greater than in the pure material, as evident from an inspection of both Fig. 1 and Fig. 6.

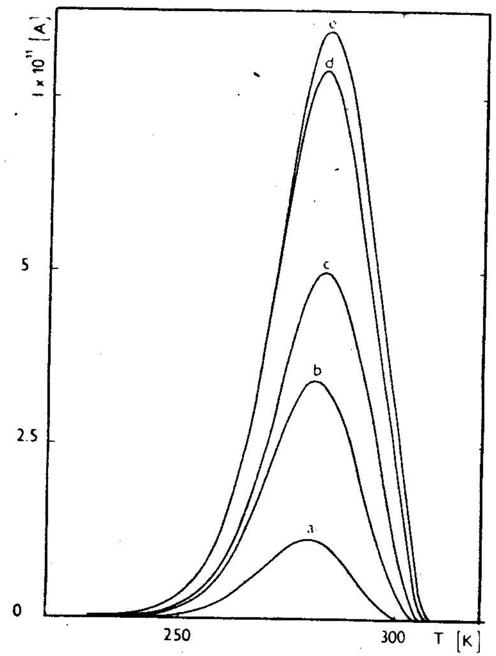


Fig. 5. $I-T$ characteristics of the system Al—As_2Se_3: 0.7 at % Al—Al biased at $T_p = 260$ K for various times t_p: a — 20 s, b — 2 min., c — 5 min., d — 10 min., e — 15 min.

2. The total charge contained in both the 280 K and the 300 K peaks in Fig. 6 is nearly equal.

As a first approximation, the observed charge Q (per unit area) is related to the density of filled states by the relation [9]

$$Q = \left|\frac{e\varepsilon N_t}{2}\right|^{1/2} \frac{V_d}{(\Delta\Psi + V_d)^{1/2} + \Delta\Psi^{1/2}} \qquad (1)$$

where $\Delta\Psi$ is the difference of the work function of glassy As_2Se_3 [24] with respect to that of the Al electrode. Then the density of states corresponding to the 280 K peak is approximately 5×10^{14} cm^{-3} and roughly equal to that of the D states, cf.

Fig. 6. If the D states are assumed to be identical with holes localized on the Se atoms, then the introduction of large amounts of Al is proposed to result in an enhanced number of broken Al—Se bonds. The Al—Se bond is expected to be partially ionic, so that the ionized Al^{+} center is probably acting as acceptor. The last conclusion concerning the nature of the Al defect is consistent with our finding that one deals with majority carriers traps.

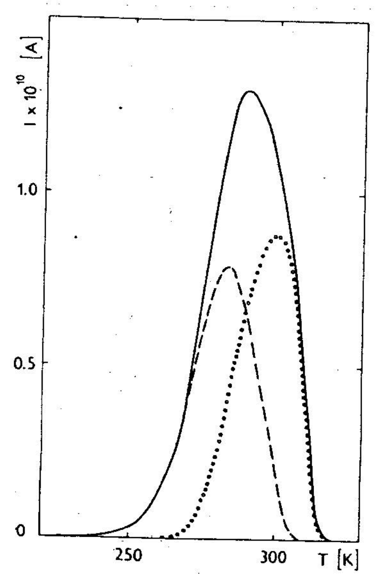


Fig. 6. Decomposition of the total DRC (full line) as a sum of the 280 K peak (dashed line) and the 300 K peak (circles), both full and dashed lines being obtained experimentally.

III. 3. Reply to some criticism

As already mentioned earlier, some doubt arose [12] concerning the interpretation of DRC in bulk As_2Se_3 by the theory of Simmons and Taylor [8, 9]. The theory had been suggested to express $I - T$ characteristics of M–I–M systems with Schottky-barriers, provided that the insulator contained a high density of defects. Then, according to Simmons and Taylor it is doubtful whether one can distinguish between surface and bulk defects acting as traps. Assuming the width λ of depletion region to be much less than the insulator thickness L, the above authors arrived at the conclusion that the current flowing in such M–I–M systems during the growth of a depletion region is a bulk-limited dielectric relaxation current.

When deriving the expression for the $I - T$ characteristic, two approaches can be utilized [9]. One can either formulate the processes in the depletion region or calculate fields and currents in the interior of the insulator. As far as there are identical traps in both contact and bulk regions, both approaches are equivalent. Simmons and Taylor [9] derived an approximate expression for the dielectric relaxation current using the former procedure, whereas Gupta and van

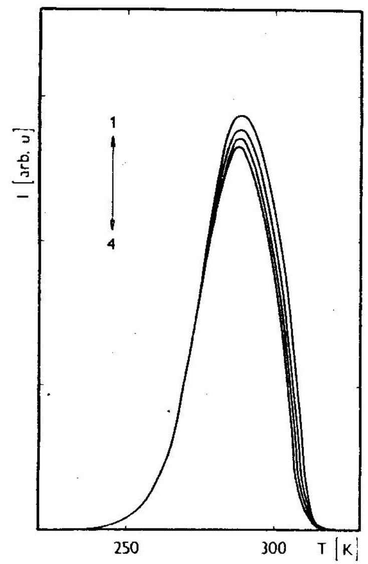


Fig. 7. Subsequent measuring cycles performed on Al—As_2Se_3: 0.7 at % Al—Al system. $T_p = 310$ K, $t_p = 5$ min.

Overstraeten [23] calculated the $I - T$ dependence applying the latter approach. It is necessary to mention that the situation introduced by Simmons and Taylor [8, 9] with the Fermi level lying exactly in the trap level is far from being a general one. In general, to maintain a possibility of the determination of the trap depth it is desirable to analyse the case when the two levels do not coincide precisely, this being the situation treated by Gupta and van Overstraeten [23].

Now let us turn our attention to the question to what extent the existing theories are applicable to our results on bulk As_2Se_3 glasses. Taking the DRC of undoped material from Fig. 1 and adopting relation (1), the density of states near the Fermi level has been estimated to be well below 10^{14} cm^{-3}. This finding makes it at least problematic to neglect completely possible differences between interface and bulk states. Moreover, macroscopic space charges are expected for such low densities of bulk defects as found, e.g., in As_2S_3 glass [25]. This seems to be a more plausible explanation for the observation that linear theories do not apply than that presented earlier [11]. Finally, there exists another circumstance which represents a serious difficulty with respect to the evaluation of DRC in As_2Se_3 glasses. Namely, near the temperature T_p (410—420 K) ionic conduction cannot be neglected [26]. Then, a space charge is expected due to mobile ions which have been blocked at the electrodes as well as that of localized electronic charges.

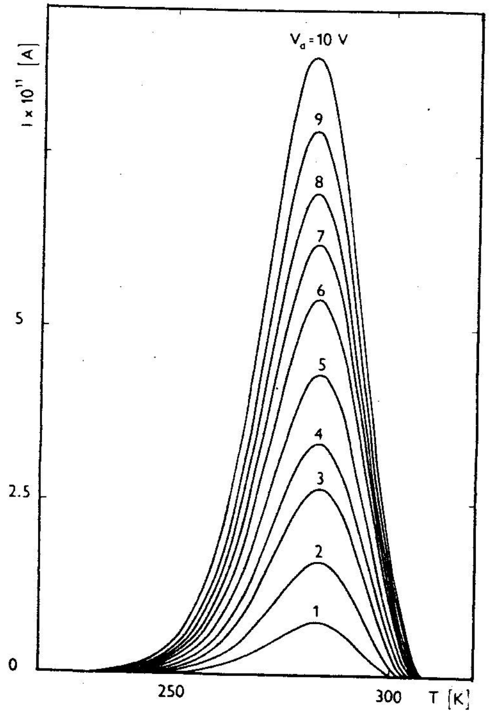


Fig. 8. Variation of both position and height of the 280 K peak due to change in bias voltage, $T_p = 260$ K, $t_p = 10$ min.

A complete treatment of this case would require mass transport equations to be satisfied, too.

We hope to have summarized most of the circumstances which represent complications arising whenever trap parameters of high resistivity solids such as As_2Se_3, As_2S_3 glasses should be obtained by thermal dielectric relaxation. In addition, when interpreting DRC in semiconductors, one should be aware of the fact that a contribution of free charge polarization can be eliminated [10]. Our observation of an almost complete annealing out of the 300 K peak by thermal treatment, not associated with thermally induced changes in the barrier height, strongly supports our interpretation of the latter peak as due to a group of metastable localized states near the Fermi level of glassy As_2Se_3.

IV. SUMMARY

As shown in the present paper, after introducing Al up to 0.1 at % into pure As_2Se_3 glass the DRC spectrum does not show remarkable changes in the sense that only the 300 K peak is observed, which is present in undoped material, too. The centres responsible for the peak have been found metastable at elevated temperatures. In common with Bishop, Strom a Taylor [15] we have ascribed them to holes localized on the chalcogens, which form centres near the middle of the gap. Residual density of these photo-induced states near 300 K is estimated to be well below 10^{14} cm^{-3}, this being probably the reason why other techniques such as optical absorption or ESR failed to detect corresponding signals at this temperature.

In glasses containing more than 0.1 at % Al an additional DRC peak could be resolved with $T_m \sim 280$ K besides the 300 K peak, the magnitude of the latter becoming greatly enhanced when compared with undoped glassy As_2Se_3. The 280 K peak has been tentatively ascribed to the formation of Al^+ ionized centres in the glass matrix, which manifest themselves as traps for majority carriers.

Exact determination of the trap parameters is not free of complexities involved mainly through the presence of ionic conduction at the temperature region where the system Al—As_2Se_3 is biased. This is certainly a disadvantage of the DRC method which is, however, partly compensated by a high sensitivity of the latter. The DRC method makes it possible to detect extremely low densities of deep traps not accessible by any other experimental method.

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Received March 10th, 1977