ON THE RELATIONSHIP BETWEEN THERMALLY STIMULATED DEPOLARIZATION (TSD) AND CONDUCTIVITY OF AMORPHOUS As_2Se_3

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The TSD peak of amorphous As_2Se_3 is shown not to be simply related to dark conductivity. Some reasons are given to search for a relation between the TSD and a group of localized acceptor-like states having energy 0·84 eV in the band gap. It is possible, that these states act as recombination centres of photoluminescence, which method also points to localized states nearly in the middle of the gap.

INTRODUCTION

Thermally stimulated depolarization method (TSD) is widely used when investigating localized states, mostly after preceding optical excitation of the material under investigation. KOLOMIEC et al. [1] found TSD maxima at 145 and 300 K, respectively, on bulk samples of amorphous As_2Se_3 provided with Al blocking contacts, having irradiated the samples during polarization. The authors [1] explained the occurrence of both maxima by localization of charge carriers in the band gap. It can be shown that the TSD peak of the bulk As_2Se_3 glass at about 300 K is observed also without optical excitation [2], polarizing sample at a sufficiently high temperature. The results could be plausibly evaluated in terms of the theory of dielectric relaxation currents [3], based on Schottky barrier formation at the interface metal-semiconductor. Using blocking and insulating electrodes, MÜLLER [4] has observed TSD of unexcited bulk As_2Se_3 with a maximum near 270 K. The measured current has been treated as a conductivity current in the field of the charge accumulated near the surface. The measurements should have demonstrated TSD in the given arrangement to be simply related to conductivity also in the case of an electronically conducting material. In the discussion it was pointed out that TSD at 300 K observed by KOLOMIEC et al. [1] may be due to equilibrium charge carriers [4].

It is the purpose of the present paper to show the preceding TSD with blocking Al contacts to be related to surface states near the equilibrium Fermi level (the maximum at 300 K). Moreover, one cannot speak about a simple relationship between TSD and conductivity in contrast to the interpretation of Müller's experimental data [4] on amorphous As_2Se_3.

EXPERIMENTAL PROCEDURE

Surfaces of bulk samples of amorphous As_2Se_3 (1 mm thick) were mechanically polished prior to the evaporation of Al contacts. One tried to prevent intense light

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exposure and oxidization of the surfaces. During depolarization the samples were short-circuited by the internal resistance of the electrometer (sensitivity 10^{-14}A/mV). All the measured samples were heated at 0·085°/s and 0·15°/s, respectively.

RESULTS

TSD of amorphous As_2Se_3 at two heating rates v are shown in Fig. 1. Well resolved current maxima are observed at 293 K and 298 K, respectively. As found earlier [2], the intensity of the maximum of the current at a given heating rate depends upon the type of the contact. This should be connected with the difference in the work function of the metal and that of the semiconductor [3]. The observed dependence (cf. [2]) would point to a group of acceptor-like energy levels, the energy at the maximum of the distribution E_m (from the valence band edge) being [3]

$$E_m = T_m\left[1{\cdot}92 \times 10^{-4} \log \frac{v}{v} + 3{\cdot}2 \times 10^{-4}\right] - 0{\cdot}015 \text{ [eV]}, \tag{1}$$

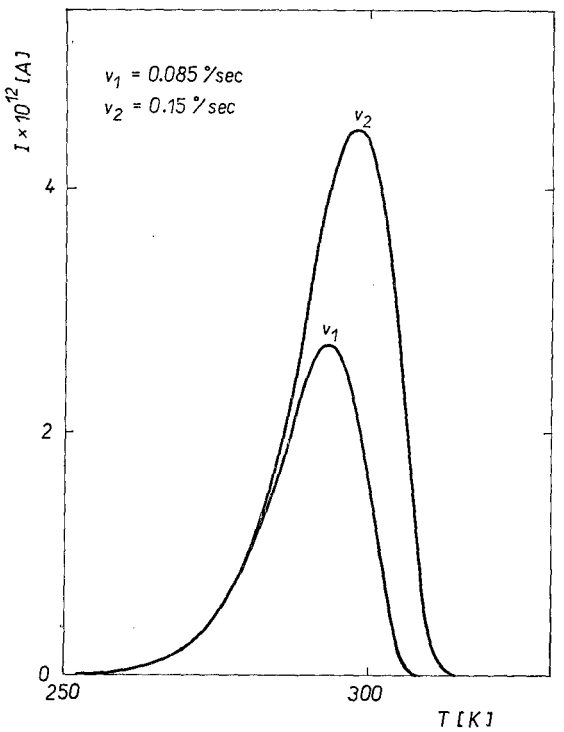

Fig. 1. TSD of the system Al–As_2Se_3–Al (0·63 × 0·89 × 0·1 cm^3), polarized for 2 minutes at T_p=300 K by a voltage 50V.

where T_m is the temperature at the maximum of relaxation current, v stands for the attempt-to-escape frequency. Applying (1) to the TSD curves in Fig. 1 one obtaines values $v \sim 10^{12}$ s^{-1} and $E_m = 0{\cdot}82$ eV, respectively. The energy determined more reliably from the initial rise 0·84 eV is in good agreement with that evaluated from (1).

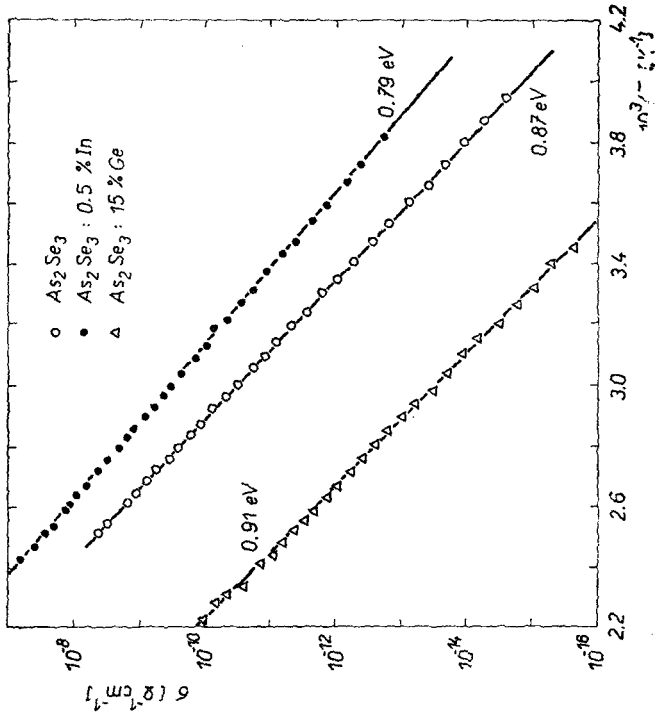

Fig. 3. dc conductivity of the investigated glasses.

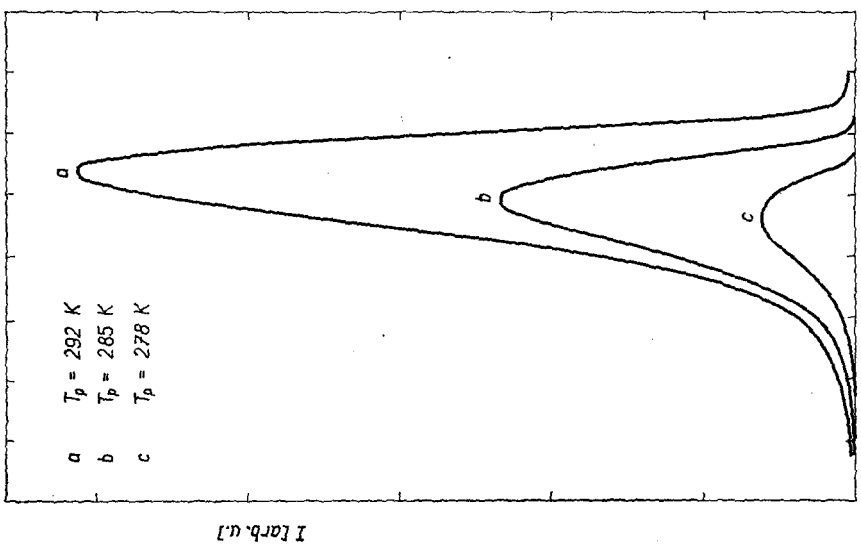

Fig. 2. TSD of the system Al–As_2Se_3–Al at various T_p.

In the case of a discrete trapping level the expected halfwidth of the peak is

$$\Delta T = \frac{2kT_m^2}{E} = 18\ \mathrm{K}\,, \tag{2}$$

the experimentally determined halfwidth (v_2 – Fig. 1) is 19 K. The curves in Fig. 1 result probably from a distribution of energy levels. As is evident from Fig. 2, the temperature at the maximum T_m is a function of the polarization temperature T_p unless a saturation is reached (a constant polarization time assumed). The energy levels lie within an interval of about 5×10^{-3} eV (cf. (17) in [3]).

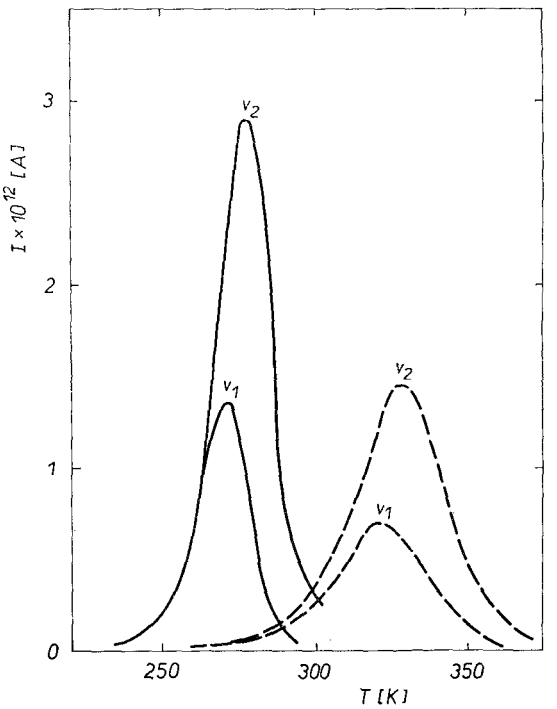

Fig. 4. TSD of amorphous As_2Se_3 + 0·5% In (full line, $T_p = 295$ K, $U_p = 50$ V), and As_2Se_3 + + 15% Ge (dashed line, $T_p = 340$ K, $U_p = 360$ V).

Table I

	E_m [eV]	E_σ [eV]	$\Delta T_{exp} - \Delta T$ [K]
As_2Se_3	0·84	0·87	1
As_2Se_3 + 0·5% In	0·71	0·79	2
As_2Se_3 + 15% Ge	0·57	0·91	2

The relationship between TSD and conductivity is evidently not as simple as stated by MÜLLER [4]. The absence of a simple relation between both phenomena follows also from the experimental results obtained on amorphous As_2Se_3 doped with In and Ge (Fig. 4). The impurities modify strongly the parameters of conductivity, as shown in Fig. 3. All results are summarized in table I.

DISCUSSION

According to our experimental results one does not observe a simple relationship between conductivity and TSD with blocking Al contacts in the case of glasses based on As_2Se_3. The apparent activation energy of TSD is always smaller than that of dc conductivity, moreover, the halfwidth of maxima is somewhat larger than expected for discrete peaks. It is remarkable that also in the arrangement with insulating electrodes the energy determined from TSD ($0{\cdot}78 \div 0{\cdot}86$ eV) is smaller than the activation energy of conductivity [4]. With respect to these facts the TSD interpretation by linear theories seems to be questionable when, moreover, only sparse evidence for deep trapping is available.

The linear theory of TSD [5] starts from the assumption that at temperature at the maximum of the current the number of the equilibrium charge carriers in the bulk exceeds by far the number of the accumulated charges, which have become free. Verifying this assumption one has to estimate the number of charges in both the bulk and the interface. As follows from the calculation [4], the number of both charges is of the same order of magnitude assuming the unusually small hole mobility $\mu_d = 1{\cdot}26 \times 10^{-7}$ cm^2/Vs, taken from the data of OWEN and ROBERTSON [6]. We suppose that it is not quite correct to estimate the concentration of equilibrium charge carriers using the mobility of the nonequilibrium ones. The drift mobility is generally assumed not to be identical with the microscopic one in the presence of trapping. Having taken the above drift mobility [6] and a Hall mobility $\mu_H = 7 \times 10^{-2}$ cm^2/Vs, NAGELS et al. [7] estimated the microscopic hole mobility at 20 cm^2/Vs, the latter corresponding well with the value calculated by BÖER [8]. It is, of course, questionable to what extent is the latter value accurate. However, the real mobility of the charge carriers is probably larger than the Hall mobility, which in most chalcogenide glasses amounts to $10^{-1} \div 10^{-2}$ cm^2/Vs. Assuming $\mu > 10^{-2}$ cm^2/Vs and $\sigma(T_m) = 4{\cdot}5 \times \times 10^{-14}\ \Omega^{-1}$ cm^{-1}, one finds the charge of equilibrium carriers in the bulk to be much less than the accumulated one ($T_m \sim 270$ K). If the activation energy of detrapping is lower than that of conductivity, and this is probably the case, the accumulated charge relaxes at a temperature when the bulk free charge concentration is still relatively small. In other words, the accumulated charge is not trapped deep enough with respect to the Fermi level when cooling the system. This might be one possible reason for the observed difference in activation energies of TSD and conductivity.

Our observations support the conclusion that surface states are responsible for the discussed TSD peaks. One cannot simply identify the surface states with localized states in the bulk. The presence of mainly acceptor-like surface states is a reason for the fact that the surface of glassy As_2Se_3 behaves as a p-type semiconductor. Microphysical nature of the localized states remains open to discussion, we believe, however, that these could act as recombination centres. Such centres were revealed by the measurements of radiative recombination [9, 10], the luminescence maximum positioned at the energies $0{\cdot}87 \div 0{\cdot}88$ eV.

CONCLUSIONS

As shown, the TSD peaks of amorphous As_2Se_3 near 300 K ($v = 0{\cdot}15°/s$) result most probably from the relaxation of the charge accumulated at the interface metal-semiconductor. We assume the accumulated charge to be trapped in localized states at low temperatures. To a distribution of localized states points unambiguously the dependence of the temperature at maximum upon the polarization temperature. The delusion of a discrete peak is due to the fact that its halfwidth is only a few degrees larger than that of a discrete peak (cf. table I).

Then the interpretation of TSD by KOLOMIEC et al. [1] seems to be correct in the sense that localized states are responsible for the maximum near 300 K in the case of amorphous As_2Se_3. A possibility to observe the discussed peak without optical excitation has been shown also by MÜLLER [4]. The identified localized states could be identical with the recombination centres of luminescence [9, 10].

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