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EFFECT OF HEAT-TREATMENT ON CARRIER MOBILITY IN CdSe

By C. Manfredotti, R. Murri and L. Vasanelli

Istituto di Fisica, Bari*

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Transport properties of CdSe samples, grown or treated in Se_2 atmosphere, are examined. In heat-treated samples the experimental mobility is lower than the theoretical one. This behaviour is attributed to a singly charged imperfection center at 0.033 eV below the conduction band. The nature and the properties of this center are discussed, according to a model proposed by Bube.

1. *Introduction*

The electrical and transport properties of semiconductors can be altered by various heat-traetment processes. As an example, the heat-treatment of CdSe in Cd or Se atmosphere is a well known method for varying the resistivity by many orders of magnitude [1-3].

We have studied very carefully the variations both in electrical and transport properties of CdSe annealed under Se_2 atmosphere. The Brooks-Herring relationship [4] for scattering due to shallow ionized donors, together with the lattice mobility expression, is unable to explain the experimental results. In order to account for the experimental mobility, we have introduced a contribution to the theoretical mobility due to the charged imperfection scattering, with occupancy changing with the temperature, as reported for photoconducting CdSe and CdS [5, 6]. By using a suitable model [5], the parameters of these scattering centers (charge, density, cross section, energy level) have been determined. These centers are certainly produced by the heat-treatment, since they are absent from the untreated samples, and do not coincide with other electron levels previously reported [7] for CdSe : Se.

2. *Experimental*

For the present measurements we started from CdSe single crystals (Semi Elements) with typical dimensions $5 \times 5 \times 0.5$ mm^3, 0.3 ohm cm resistivity and 500 cm^{2}V^{-1}s^{-1} the Hall mobility at room temperature. They were encapsulated in evacuated (10^{-4} mmHg)

* Address: Istituto di Fisica, Via Amendola 173, 70126 Bari, Italy.

fused silica ampoules, together with an excess of Selenium, so that a saturated amtosphere could be attained.

A low annealing temperature (400°C) was chosen, in order to avoid troublesome effects such as enhanced sublimation (reservoir method) or too high Se_2 pressures, which lead to non uniformities in resistivity [8]. Annealing time ranged between 2 and 40 hours [2]. After the annealing process, the samples were quenched at room temperature and finely polished. Their resistivity and the Hall mobility were measured between 50 and 300°K, in a magnetic field of 18 KG, by means of the Van der Pauw method [9], slightly modified in order to avoid thermogalvanomagnetic effects [10].

3. *Results*

In agreement with previously reported results [12], we noticed a strong increase in resistivity, together with a decrease in the mobility, as a function of the annealing time; after 5 hours, resistivity and mobility reached constant values as high as 10^8 ohm cm and as low as $50\ cm^2V^{-1}s^{-1}$, respectively. It is worthwhile to note that these are exactly the properties of CdSe grown from vapour [11, 12]. We also checked that these were true bulk properties, by repeated measurements on the same samples lapped down to the half of the original thickness. We report, here, the average results obtained on some samples, the properties of which were measured both before and after two hours annealing.

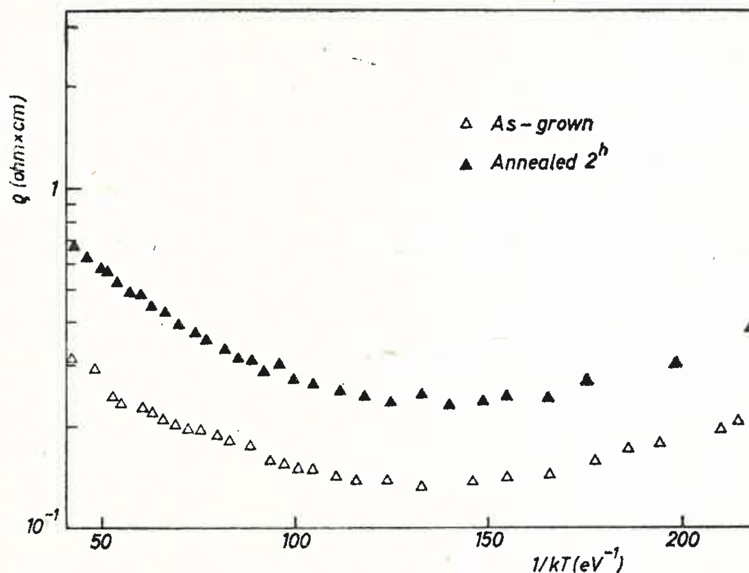

Fig. 1. Typical resistivity behaviour versus $1/kT$ for treated and untreated samples

The temperature dependence of resistivity and of electron concentration are shown in Figs. 1 and 2, respectively. The solid lines represent a computer fit obtained with the single donor–single acceptor model [13], using the density-of-states effective mass of the

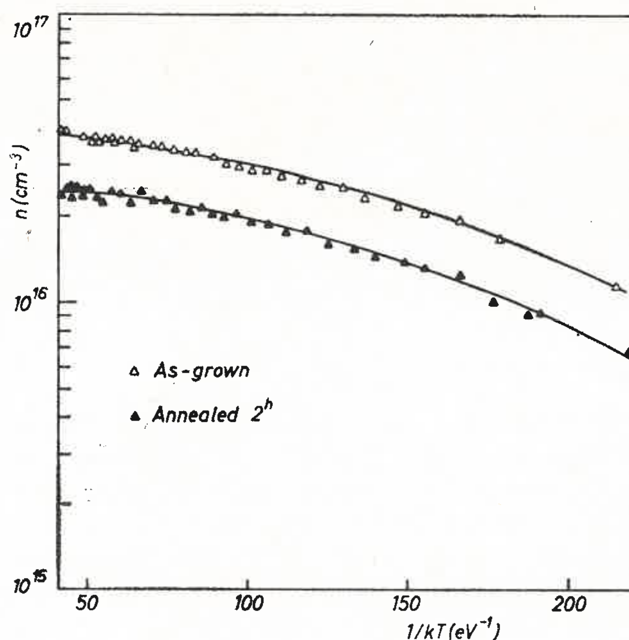

Fig. 2. Electron concentrations versus $1/kT$ for the same samples of Fig. 1

conduction band (m^*), donor and acceptor concentration (N_D, N_A) and donor ionization energy (E_D) as parameters. The values obtained for these parameters are reported in Table I.

TABLE I

Typical value of N_D, N_A, E_D and m^*/m_0 for the untreated sample and for samples annealed for two hours at 400°C. The values were obtained by fitting the experimental Hall data to the single donor-single acceptor model

Samples	N_D (cm^{-3})	N_A (cm^{-3})	E_D (eV)	m^*/m_0
As-grown	5.4×10^{16}	1.4×10^{16}	0.011	0.24
Annealed 2^h	3.5×10^{16}	1.0×10^{16}	0.013	0.25

One can note that, while the donor concentration decreases during the heat-treatment, the acceptor concentration remains practically constant, and therefore compensation effects do not seem to be important in the first stages of the annealing. The decrease in donor concentration is consistent with the variation of the donor ionization energy. The value of m^* is larger than obtained by other methods [14], but it agrees with a previous

determination based on the Hall effect [15]. The donor energy level at 0.013 eV was previously reported [3] and attributed to cadmium interstitials.

The Hall mobility dependence on temperature is shown in Fig. 3 (untreated samples). The solid curve represents the theoretical mobility accounting for all scattering mechanisms

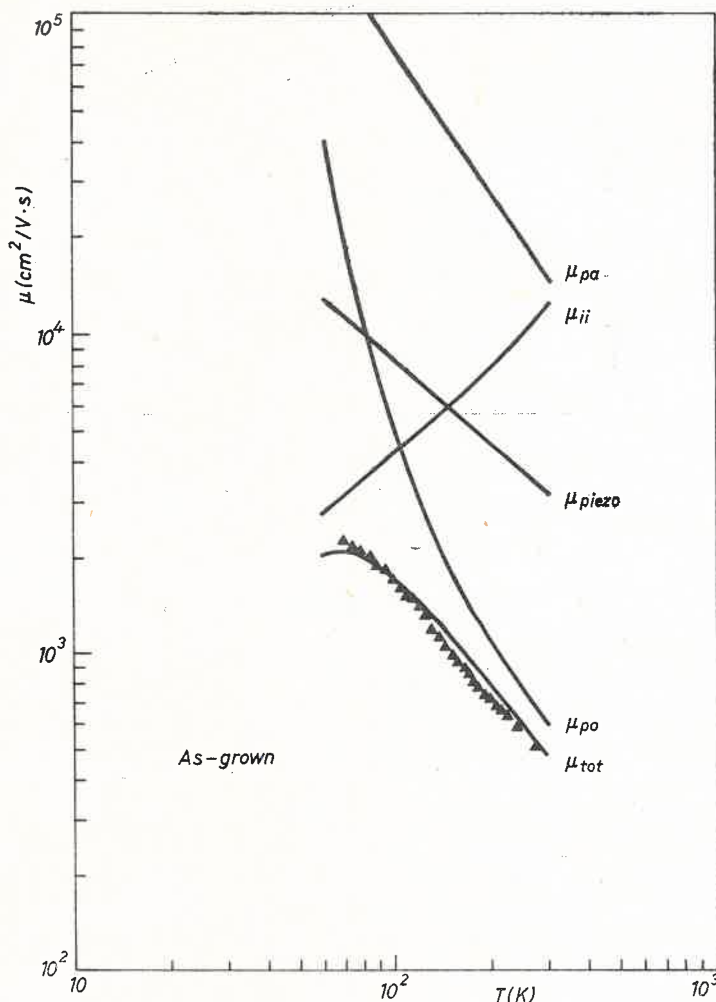

Fig. 3. Hall mobility dependence on temperature for untreated sample of Figs. 1 and 2. Theoretical value of the polar optical mobility (μ_{po}), piezoelectric mobility (μ_{piezo}), deformation potential mobility (μ_{pa}), ionized impurity mobility (μ_{ii}) and total mobility (μ_{tot}) are reported

active in CdSe: polar optical phonon scattering [16], piezoelectric scattering [17], deformation potential scattering [18] and ionized impurity scattering [18]. No adjustable parameters were used in computing mobility: the values of n, N_A, N_D and m^* were taken from the previous fittings; all other constants were taken from literature [3, 19]. The

agreement between experimental and calculated Hall mobility is very good. However, in the case of the annealed samples, the experimental mobility was considerably lower than the theoretical one, Fig. 4.

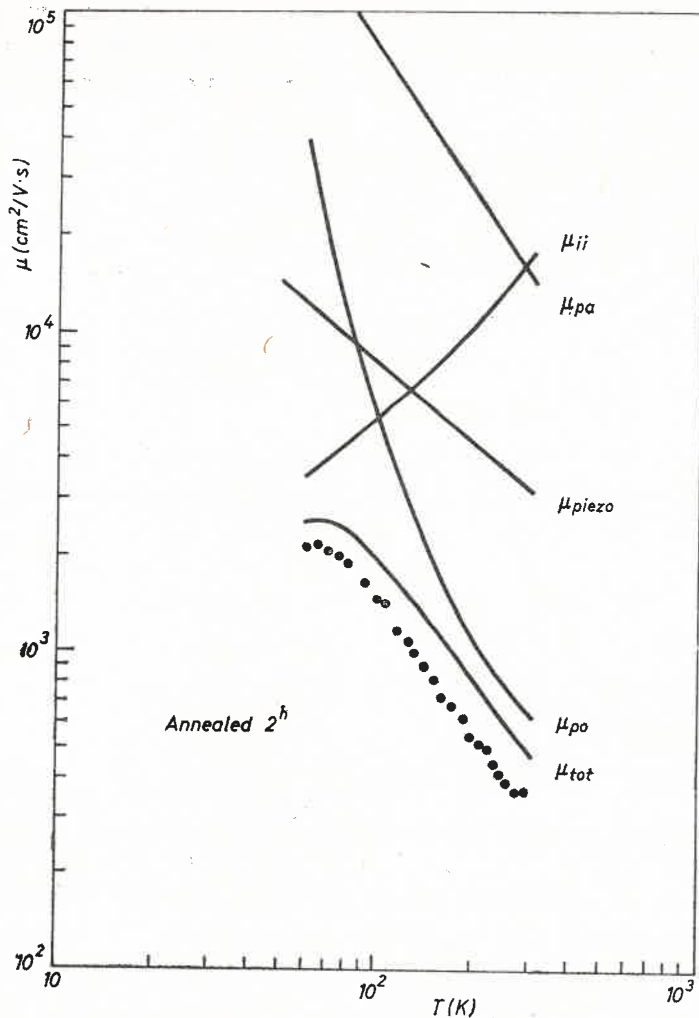

Fig. 4. Hall mobility dependence on temperature for treated sample of Figs. 1 and 2. For symbols, see Fig. 3

4. *Discussion*

The behaviour of the mobility can be due either to the presence of inhomogeneous regions and to the associated space-charge regions [20], or to the presence of relatively deep centers with a large scattering cross section. The former possibility was rejected because, in our case, the dependence of residual mobility on temperature and carrier concentration ($\mu_s \cong n^{-4/3}\,T^{-5/6}$) is in strong disagreement with the model suggested by Gossick ($\mu_s \cong n^{1/3}T^{-5/6}$) [21].

Therefore, we took into consideration the latter possibility and introduced the model suggested by Bube [5]. This model associates a change in mobility with a change in the occupancy of an imperfection center, as a consequence of a displacement of the Fermi level. We chose case (a) of Ref. [5], which assumes the existence of a positively charged imperfection center lying above the Fermi level at high temperature and below the Fermi level at low temperature. In effect, by plotting the reciprocal of the residual mobility as

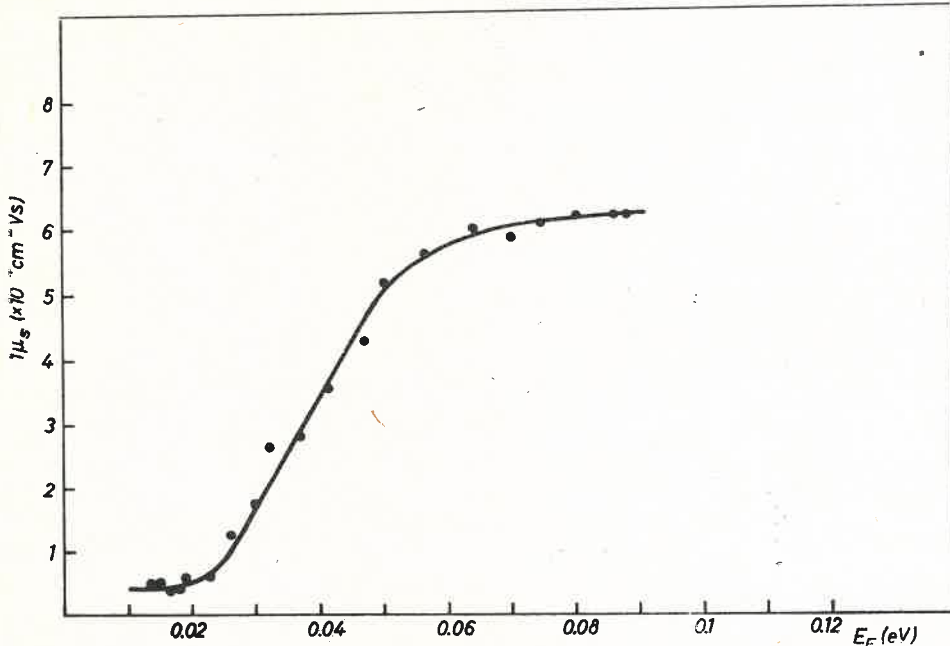

Fig. 5. Reciprocal of the residual mobility versus the Fermi level energy for treated samples

a function of the Fermi level E_F, we obtained exactly the behaviour expected from the model in this case, Fig. 5. According to the theory, the difference between $1/\mu_s$ for small E_F and large E_F gives $\beta v S_+ N_+$, where β is a proportionality factor between mobility and time between scatterings, v is the thermal electron velocity, S_+ is the scattering cross section and N_+ the density of imperfection centers. In our case, $S_+N_+ = 7.3\ 10^4\ \mathrm{cm}^{-1}$. The depth of the center E_+ can be calculated taking into account that, at $E_F = E_+, \Delta(1/\mu_s) = \beta v S_+ N_+/3$. In our case, $E_+ = 0.033$ eV. The slope of the curve in Fig. 5, at $E_F = E_+$, is $1.5\ 10^{-2}$ in satisfactory agreement with the value which could be calculated from the theory: $2\beta v S_+ N_+/(9kT)$. The density of these centers at 0.033 eV can not be obtained from the present measurements. However, assuming that their density is of the order of $10^{15}\ \mathrm{cm}^{-3}$ (value not unrealistic), one can derive a capture cross section of about $10^{-10}\ \mathrm{cm}^2$. There fore, they should be classified as "giant scattering centers". It is almost impossible to ascertain, on the basis of the present results the nature of these centers at 0.033 eV. The fact, that the μ_s is still finite for E_F around 0.015 eV suggests that other shallower centers

affect the mobility. They can not be indetified with the donor at 0.013 eV, since this effect is absent in untreated CdSe: more probably it should be identified with the shallow level at 0.010 eV found in CdSe : Se [6].

5. Conclusion

Summarizing, the conclusions are the following ones: (1)the first stages of the annealing of CdSe under saturated Se_2 atmosphere are characterized by a decrease in shallow donor concentration. These donors, which are at 0.013 eV below the conduction band, are generally ascribed to singly ionized Cd interstitials [3]. Probably, this effect is due to the rapid diffusivity of the Cd_i at low partial pressures [22]. (2) An imperfection center is formed at 0.033 eV below the conduction band. This center is singly charged, and has a (capture cross-section)×(density) product $S_+N_+ = 7.3\ 10^4\ cm^{-1}$. This center is responsible for the behaviour of the Hall mobility in annealed samples, in the sense that its occupancy changes with the temperature. (3) Finally, the model proposed by Bube [5], in order to explain mobility anomalies in photoconductors, seems valid and suitable for heat-treated semiconductors, and it can be applied not only to the photo-Hall mobility measurements, but also to the usual mobility measurements as a function of the temperature.

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