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ENERGY SPECTRUM AND NATURE OF TRAPPING CENTERS IN SINGLE CRYSTAL CdSe FILMS

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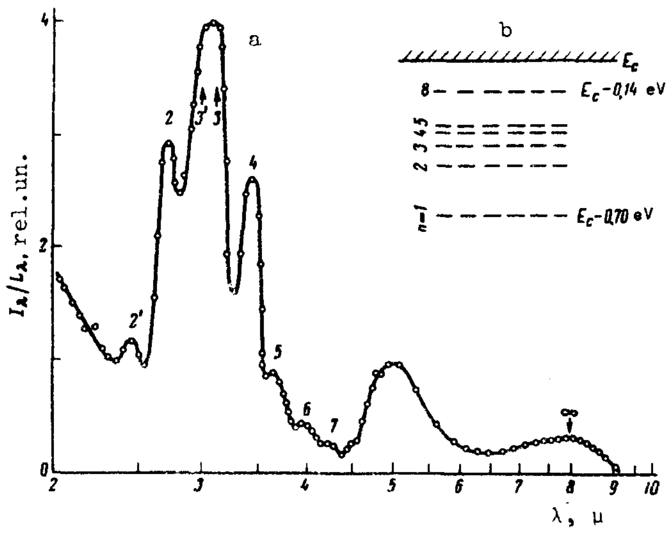
The most important problem in the investigation of trapping centers in semiconductors is to establish their nature. In spite of the considerable number of investigations performed for this purpose on II - VI semiconductors, the concrete physical and chemical nature of the trapping centers is still unknown. The lack of reliable information on the structure of these centers does not make it possible to interpret a number of experimental results, particularly the existence in semiconductors of a large number of levels of traps whose spectra can be discrete as well as quasicontinuous [1, 2].

We present here data on the investigation of traps in single-crystal CdSe films with wurtzite structure, by the method of induced impurity photoconductivity (IIP), and the results of their analysis. The technology of film production is described in [3], and the procedure of measuring the IIP is given in [4].

Under the usual conditions, the photoconductivity in CdSe films is observed in the region of their intrinsic absorption. Preliminary photoexcitation of films in this region, at 95°K, leads to the appearance of IIP due to optically excited electrons with non-uniformly filled trapping levels, in the interval 1 - 9 μ (curve a in the figure). We see on the IIP curves of the investigated films a number of bands with different half-widths, indicating that the traps have a complicated energy spectrum.

To identify the IIP peaks it is assumed that CdSe contains in addition to isolated trapping centers also pairs consisting of a trapping center and a shallow ionized donor. The trapping centers and the donors are distributed over the anion and cation sites, respectively. In the sphalerite lattice the



a) Spectral distribution of IIP in single-crystal CdSe films. b) Scheme of trapping energy levels due to the presence of CdSe of pairs from anion vacancies and donors in the cation sites. The integers on the figure denote the numbers of the coordination spheres, and the primed figures are the numbers of additional coordinate spheres in the wurtzite lattice, unlike the sphalerite lattice.

distance between sites is $r_n = a[(n/2) - (5/16)]^{1/2}$ (a is the lattice parameter, n = 1, 2, ... ∞) [2]. In the wurtzite lattice r_n takes on also a number of additional values (4.4 Å, 6.2 Å, etc.), owing to the realization of additional coordination spheres in this structure.

The ionization energy of a trapping center paired with a donor can be given by the formula

$$E_{tn} = E_{t\infty} + \frac{e^2}{\varepsilon r_n}, \tag{1}$$

where $E_{t\infty}$ is the ionization energy of an isolated trapping center, and $e^2/\varepsilon r_n$ is the shift of the level $E_{t\infty}$ as a result of the proximity of a positively charged donor, and is equal to the proposed shift of the acceptor level in the donor-acceptor pair [5, 6].

According to (1), the spectrum of the traps contains a series of discrete levels, which merge with a continuum bounded by the value $E_{t\infty}$ (Fig. b). $E_{t\infty}$ should correspond to the long-wave edge of the IIP, located near 0.14 eV, under the condition that expression (1) describes correctly the experimental ionization-energy spectrum of the traps (E_t).

Knowledge of $E_{t\infty}$ makes it possible to compare E_t with E_{tn}. This comparison is given in the table for deep levels responsible for well-resolved peaks (n = 2', 3', 2 - 7) at λ_m = 2.45, 2.74, 3.07, 3.4, 3.68, 3.9, and 4.15 μ[1]) (the broad bands on the IIP curves in the region λ > 4.5 μ are apparently due to superimposed higher-order levels, the distances between which are much smaller than their half-widths). The values of E_t were determined from the extrapolated long-wave boundary of each band, which was shown, by a reduction of IIP curves obtained for a large number of samples, to be located at a distance 0.03 eV (±0.005) from the maximum point. In the calculations of E_{tn} we used ε = 9.6 and a = 6.05 Å [2]. We see from the table that there is good agreement[2]) between the distributions of the levels in the calculated and experimental spectra.

The traps with E_t = 0.14 eV, observed many times in investigations of TSC both in CdSe [7, 9, 10] and in CdS [11 - 15], are connected with anion vacancies (V_A) [9 - 13]. The agreement between the values of E_t may be due to the fact that these vacancies are identical in CdS and CdSe. Shallow donor centers in pairs are apparently produced by residual impurity atoms. These impurities are most likely donors of group III replacing the Cd in the CdSe lattice [2].

It can be concluded that the trapping centers in the CdSe films are connected with vacancies V_A paired with shallow donors. From this trap model we draw the following important conclusions:

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1) The band with the peak at λ_m = 3.07 μ has a much larger half-width (0.05 eV) than the neighboring bands (0.03 eV). This indicates that this band has a doublet structure (n = 3', 3).

2) It is also seen from the table that the thermal values of E_t, estimated by the TSC method in CdSe crystals [7], agree with the optical values. IIP was observed in crystals in the region λ < 4 μ [8].

Calculated (E_{tn}) and experimental (E_t) values of the trap ionization energy in single-crystal CdSe films. The last row shows for comparison the values of E_t, determined by the method of thermostimulated conductivity (TSC) in CdSe crystals [7].

n	2′	2	3′	3	4	5	6	7	∞
E_{tn}, eV	0.48	0.44	0.385	0.37	0.33	0.31	0.29	0.275	0.14
E_t, eV	0.48	0.43	≈ 0.38	0.37	0.33	0.31	0.29	0.27	0.14
E_t, eV	–	0.43	–	0.37	–	0.31	–	–	0.15

1) Depending on their nature, the shallow donors in II-VI semiconductors occupy not only cation sites but also anion sites [2]. One should therefore observe in such semiconductors, in addition to the trap spectrum described in the present paper, also the spectrum due to pairs made up of the vacancies V_A and a donor in an anion site.

2) Since the values of ε and $\underline{a}$ in the compounds CdS_xCdSe_{1-x} ($x = 0 - 1$) are close, and the V_A centers identical, such compounds, when prepared by an identical technology, should have similar trap spectra. Investigations of IIP in CdS_xCdSe_{1-x} films show that these conclusions are confirmed.

Thus, the experimental data offer evidence of realization of pairs of components of the donor type in CdS_xCdSe_{1-x} semiconductors. We note that the pairs produced as a result of clustering of donors have been observed also in Ge and Si (see [5]).

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