Semiconductor Physics, Quantum Electronics & Optoelectronics. 1999. V. 2, N 1. P. 31-34.

PACS 78.66.H; UDK 535.34,621.315.592

Saturation of optical absorption in CdS single crystals

N. I. Malysh, V. P. Kunets, S. I. Valiukh, Vas. P. Kunets
Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, Kyiv, 252028, Ukraine, phone 265 62 82

Abstract. The absorption saturation of CdS single crystals was investigated in the Urbach region. It was shown that the threshold behaviour of the absorption coefficient is caused by recharging of the shallow acceptors, and the absorption edge has exponential character both at low and high pumping intensities. The calculation method of nonlinear transmission dependencies was proposed. Using the known formulae one can minimize the value of root mean square deviation of the measured data from the calculated ones in the whole region of the light intensities.

Keywords: absorption, saturation, recharging, acceptor.

Paper received 01.12.98; revised manuscript received 31.03.99; accepted for publication 19.04.99.

The optical absorption saturation (OAS) in semiconductors was observed in band-to-band [1], exciton [2] transitions and in transitions to band tail states [3]. In the first case OAS was explained by the occupation of the extrema of allowed bands with nonequilibrium charge carriers (the dynamic Burstein-Moss effect), in the second case, it was a result of competition between several mechanisms, such as the occupation of the states within bands, the multi-body interaction between free carriers, screening of excitons and others. And the third case was attributed to recharging the charged defects responsible for formation of Urbach absorption edge.

Previously we have investigated in details the nonlinear absorption of CdSe single crystals in a broad spectral range of the fundamental absorption edge [3, 4]. In this paper the OAS in CdS was studied in the Urbach part of the absorption edge. Accounting similarity of the physical properties for these semiconductors, it can be assumed that the features of the non-linear absorption in them are also similar. This work is aimed to check this assumption.

The samples of intentionally undoped 50-300 μm thick CdS single crystals were investigated. Pumping was carried out using dye-laser with the spectral range of 450-750 nm, line halfwidth of 0.5 Å and pulse duration 6 ns. The valence band of hexagonal direct-bandgap CdS is split by the crystal field and spin-orbit interaction into three subbands. The transition from the upper subband to the conduction band is allowed in the polarization $\vec{E} \perp C$, and the transitions from two lower subbands are allowed in polarizations $\vec{E} \perp C$ and $\vec{E} \parallel C$. Hence, investigations both polarizations of the laser light in respect to the crystal optical axis were used.

In the whole investigated spectral range of the CdS absorption edge for polarizations $\vec{E} \perp C$ and $\vec{E} \parallel C$ the dependence of transmission, T, on the light intensity, I, has the form similar to that presented in Fig. 1. It can be seen that at weak light fluxes (section I) T does not depend on I up to some critical value, starting from which a sharp increase of transmission is observed (section II) followed by the gradual approach to the saturation at high intensities (section III). In this case, the same as in CdSe single crystals, transmission does not reach the limitation level due to Fresnel reflection, which indicates that the residual (non-photoactive) absorption is present.

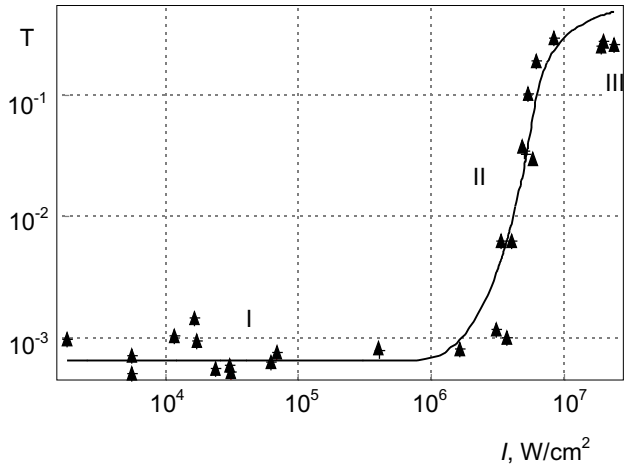

Fig. 1. Typical dependence of transmission of CdS on the intensity of excitation irradiation. Dots represent the experimental curve and the line is the calculation result according to equations (1)-(3). The thickness of the sample is 257 μm, excitation wavelength is 5163 nm, $\vec{E} \perp C$.

In stationary mode of exciting the semiconductor in the region of band-to-band or impurity-to-band transitions, OAS can be described in frames of the two-level model [1]. In the Urbach region of the spectrum, however, the two-level model does not provide satisfactory description of OAS. In this case, a satisfactory agreement with the experiment can be achieved by using the phenomenological model [5], assuming that at some critical value of the non-equilibrium carrier concentration the step-like reduction of the absorption coefficient K occurs from the initial value K_H to the final value K_B. Under these conditions near the illuminated face of the sample the domain of bleached part of the volume is formed, which moves to the opposite face. In this case, with account of Gaussian distribution of intensity across the laser beam cross-section, for three characteristic parts of intensities the non-linear dependence T(I) can be described analytically by the set of three equations [5]:

$$T = (1-R)^2 \exp(-K_H d), \qquad I \le I_\ell \tag{1}$$

$$T = (1-R)^2 \exp\left(-K_H d\right)\left(\frac{I_l}{I_0}\right)\times\left[1+\frac{K_B}{K_H}\left(\frac{I_0}{I_l}-1\right)\right]^{K_H/K_B}, \qquad I_\ell \le I \le I_h \tag{2}$$

$$T = (1-R)^2 \exp\left(-K_H d\right)\left(\frac{I_l}{I_0}\right)\times\left[1+\frac{K_B}{K_H}\left(\frac{I_0}{I_l}-1\right)\right]^{K_H/K_B}, \qquad I > I_h \tag{3}$$

where R is the reflectivity, I_ℓ, I_h are intensities related to the beginning and the end of the bleaching process, respectively. The two latter magnitudes are connected with each other by the equation:

$$I_h = A I_l = \left\{1+\frac{K_H}{K_B}\left[\exp\left(K_B d\right)-1\right]\right\} I_l. \tag{4}$$

The equations (1)-(4), in principle, make it possible to calculate the $T(I)$ dependencies and to compare them with experimentally measured ones, as it was done in the paper [5]. The method of this calculation is based on the fact that all the intensity interval can be divided conditionally into three above mentioned parts: of low, intermediate and high intensities (Fig. 1). In this method, in the first section, the only fitting parameter K_H is used for the calculation of transmission. In the second and third sections, as far as independent fitting parameters K_B and I_ℓ are used. The first one (K_B) can be estimated approximately from the experimental value of transmission in the third section, that is at high intensities (Fig. 1, section III). The second one (I_ℓ) is estimated from the intensity corresponding to the intensity change by a factor of e. Then, by variation of these two parameters the fitting of the calculated curve to the experimental one is carried out. The fitting quality in this technique is assessed by the best visual coincidence of the calculated curve with the experimental dependence. This is a drawback of the above technique, since the mathematical criterion describing the degree of coincidence of the theoretical curve with the experimental one is absent. The second drawback is the calculation complexity.

In this paper another method is suggested for the calculation of the $T(I)$ dependence which makes it possible to adjust the calculated curve to the experimentally measured one using the least-mean square technique with the help of modern personal computers. In this method, for every experimental value of transmission the abnormality coefficient is calculated and random values are neglected [6]. The essence of this method consists in the following.

The measured dependence $T(I)$ is approximated by the function determined by the equations (1)-(3). By analogy with the well-known and widely used least-squares method (LSM) [7, 8] the unknown parameters are determined from the condition of minimization of the weighted mean least-square error [6]:

$$\sigma^2 = \sum_{k=0}^{m} \gamma_k \left(F\left(K_H, K_B, I_\ell\right) - y_i\right)^2 \tag{5}$$

where $F(K_H, K_B, I_\ell)$ is a function given by equations (1)-(3), y_i is the experimental value of the sample transmission at intensity I_i, γ_k are set positive weight coefficients. The coefficients γ_k should necessarily be introduced because absolute magnitudes of measurement errors depend strongly on the intensity of light, I.

Unlike the conventional methods for the determination of unknown coefficients based on the approximation of the calculated curve by the polynomial regres-

sion or by the set of orthogonal functions, in this problem some difficulties arise related to a rather cumbersome form of the function $F(K_H, K_B, I_\ell)$. In the conventional LSM one should take the particular derivatives of the function (1)-(3) in respect to unknown parameters and equate them to zero. Then by solving the obtained set of equations the sought coefficients should be determined. However, this method is not the best one, since in this case a set is obtained of three nonlinear equations which are very complicated and do not provide a correct solution at wrong setting of initial approximations. In the described method the function σ^2 is constructed according to the equation (5) depending parametrically on the values of K_H, K_B, I_ℓ. Then, using the direct search minimization technique [8, 9] and setting the initial approximations for K_H, K_B, I_ℓ, the minimum of σ^2 is found. To obtain the global minimum, the extremum searching procedure is repeated at different values of initial approximations. After that, the minimum value is chosen from all previously obtained values of σ^2 which corresponds to the global minimum. The advantage of this technique is that all unknown fitting parameters are determined from the condition of the lowest value of σ^2 in the *whole intensity interval*, and not in separate parts of it, as was done previously [5]. Besides, this technique makes it possible to use modern personal computers for fitting, hence the calculation process may be automated and the time of parameter determination can be reduced essentially.

To exclude random data from the initial selection the assessment of abnormality of all measured results is carried out [6]. The coefficient of abnormality V_i is calculated from the equation

$$V_k = \left| y_i - F(K_H, K_B, I_\ell) / \sigma \right|, \qquad (6)$$

where the value of function $F(K_H, K_B, I_\ell)$ is determined at $I = I_i$, and compared with the reference data [6]. At large values of V_i, the y_i value is considered as the outlier and the calculation is repeated with this point being removed.

The calculated in such a way curves agrees quantitatively well with the experimental results (Fig. 1). This fact proves that blooming in CdS, the same as in CdSe, is described by the phenomenological model [5] and is related to recharging of shallow acceptors. In calculations of the dependence $T(I)$ for CdS in frames of the two-level model the satisfactory agreement of the calculation with the experiment was not achieved. This fact proves again that the OAS mechanism in the Urbach part of the CdS spectrum is not related to occupation of empty states in the respective band tails with the non-equilibrium charge carriers. Experimental dependencies $T(I)$, measured at the set of wavelengths allow us also to determine the values of K_H and K_B and to establish the spectral dependence of the absorption edge in CdS at low ($I < I_\ell$) and high ($I > I_\ell$) intensities. In both cases it has an exponential character (Fig. 2) corresponding to the Urbach rule.

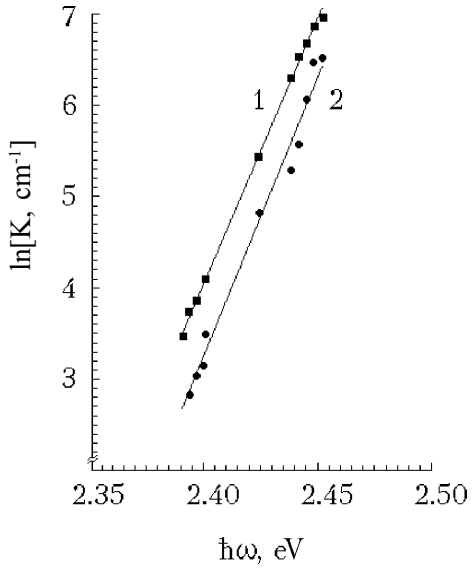

Fig. 2. Spectral dependencies of absorption coefficient in CdS at low (1) and high (2) intensities. $\vec{E} \perp C$.

Thus, in the Urbach region of the spectrum of CdS single-crystal the sharp decrease of the absorption coefficient was found at high intensities of laser irradiation. It can be satisfactorily described in frames of the phenomenological model of shallow acceptor recharging, when anomalously fast reduction of the absorption coefficient occur. This is confirmed by the similar character of absorption saturation processes in both semiconductors. Spectral dependencies of linear and non-linear absorption coefficients obey the exponential law.

References

1. V. P. Gribkovski, Teoriya pogloshcheniya i ispuskaniya sveta v poluprovodnikakh (Theory of absorption and emission of light in semiconductors), Nauka i Tekhnika, Minsk (1975) (in Russian).
2. I. Broser, J. Gutowsky, Optical nonlinearity of CdS // *Appl. Phys. (b)*, **46**, p. 1-17 (1988).
3. N. R. Kulish, M. P. Lisitsa, N. I. Malysh, B. M. Bulakh, Nelineinost' kraevogo pogloscheniya CdSe (Nonlinearity of edge absorption in CdSe) // *FTP*, **24**(1), p. 25-28 (1990) (in Russian).
4. B. M. Bulakh, B.R. Djumaev, N. E. Korsunskaya et al., Vliyanie otzhiga v parakh sobstvennykh komponentov na pogloschenie sveta v oblasti Urbakhovskogo kraya CdSe (Influence of annealing in the vapour of intrinsic components on the light absorption in the Urbach edge region of CdSe) // *FTP*, **25**(11), p. 1946-1951 (1991).
5. N. R. Kulish, N. I. Malysh, V. N. Sokolov, Prosvetlenie monokristallov CdSe v oblasti kraya sobstvennogo pogloscheniya pri neodnorodnom fotovozbuzhdenii (Blooming in CdSe single crystals near the intrinsic absorption edge at nonuniform photoexcitation) // *Kvantovaya Electron*., s. 38, p.66-82, Kiev (1991).
6. K. G. Rego, Metrologicheskaya obrabotka rezultatov tekhnicheskikh izmereniy (Metrological processing of results of technical measurements), Tekhnika, Kiev (1987) (in Russian).
7. A. B. Bartkiv, Ya. T.Grynchishin, A. M. Lomakovich,Yu. S. Ramskiy, Turbo Pascal: algoritmy i programy: chiselni metody v fizyt-

si ta matematytsi (Turbo Pascal: algorithms and programs: numerical methods in physics and mathematics), Vishcha Shkola, Kiev (1992) (in Ukrainian).
8. V. P. Dyakonov, Spravochnik po algoritmam i prgrammam na yazyke beisik dlia personalnykh EVM (Manual on algorithms and programs in the Basic language for PC), Nauka, Moscow (1987) (in Russian).
9. H. -I. Kunze. Metody fizicheskikh izmereniy (Methods of physical measurements), Mir (1989) (Russian translation).