Available online at www.sciencedirect.com
SCIENCE DIRECT
ELSEVIER
Physica B 340–342 (2003) 258–262
PHYSICA B
www.elsevier.com/locate/physb

Redistribution of mobile point defects in CdS crystals under ultrasound treatment

L.V. Borkovska[a,*], M.P. Baran[a], N.O. Korsunska[a], I.V. Markevich[a], O.F. Singaevsky[a], M.K. Sheinkman[a], T.V. Torchynska[b]

[a] *V. Lashkaryov Institute of Semiconductor Physics NASU, 45 Prospect Nauky, Kyiv 03028, Ukraine*
[b] *ESFM-Instituto Politecnico Nacional, 07738 Mexico D.F., Mexico*

Abstract

In CdS crystals, the influence of ultrasound (US) pulses on photocurrent, thermally stimulated current and edge emission spectra was observed. The effect was found to intensify with dislocation density. The analysis of obtained results showed that US treatment resulted in the decrease of shallow donor density in crystal bulk and its increase in near dislocation regions. This process of donor gettering by dislocations was shown to be one of the mechanisms of electron-beam-pumped CdS-based lasers degradation.

Keywords: Point defects; Ultrasound; Dislocations

1. Introduction

It is known that the influence of ultrasound waves on semiconductor can cause considerable change in its defect system [1]. Depending on ultrasound (US) intensity U two groups of effects are observed. When U exceeds some threshold value U_{th}, multiplication of dislocations and creation of new point defects take place [1,2]. At $U<U_{th}$ defect redistribution and transformation, such as dissolving of clusters, defect annihilation, metastable-to-stable state transfer, enhancement of defect diffusion and gettering of defects by dislocations occur [1].

In CdS crystals, the decrease of the density of cadmium interstitials Cd_i in crystal bulk under subthreshold US treatment had been earlier found [3]. This effect had been supposed to be due to gettering of shallow donors Cd_i by vibrant dislocations [1,3]. In the present paper some proofs for this model were obtained and a new effect, namely, the influence of US on the shape of edge green emission spectrum was found.

2. Experimental procedure and results

Nominally undoped bulk CdS crystals grown by sublimation were investigated. The samples of typical dimensions $10\times5\times2\,mm^3$ were cut from large boules and were supplied with In electrodes. The density of dislocations N_D was calculated

*Corresponding author. Fax: +380-44-265-8344.
E-mail address: bork@lumin.semicond.kiev.ua (L.V. Borkovska).

0921-4526/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2003.09.077

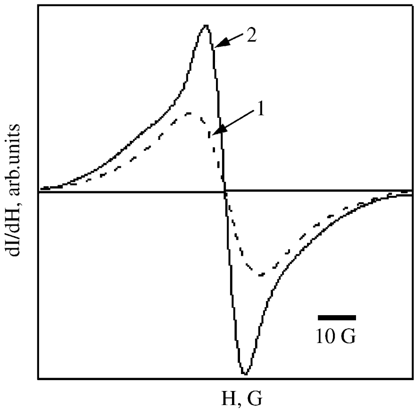

Fig. 1. Dark (1) and photo-EPR (2) signals caused by shallow donors in CdS crystals with $N_D = 5 \times 10^5\,cm^{-2}$, $T = 20\,K$.

Fig. 2. EBIC image of CdS crystal with $N_D = 5 \times 10^5\,cm^{-2}$.

from the number of etch pits on (0 0 0 1) plane. In as grown crystals from different bouls N_D varied in (10^2–10^6) cm^{-2} range.

When direct voltage was applied to the samples, they displayed high resistivity ($\rho \geqslant 10^8\,\Omega\,cm$). At the same time EPR measurements indicated that investigated crystals contained low-resistivity inclusions. The evidence of this was the presence of dark EPR signal caused by shallow donors side-by-side with photo-EPR one (Fig. 1). Detailed description of the technique and results of EPR investigations see in Ref. [4]. The analysis of EPR spectra showed that the density of shallow donors in low-resistivity regions exceeded $10^{17}\,cm^{-3}$, whereas that in high-resistivity crystal bulk was about $10^{16}\,cm^{-3}$ [4]. The relative intensity of dark EPR signal depended on N_D: in crystals with $N_D = 10^2 - 10^3\,cm^{-2}$ this signal was practically absent, and at $N_D = 10^6\,cm^{-2}$ it was the greatest.

To ascertain the shape and size of low-resistivity regions, investigation of electron beam induced currents (EBIC) was performed. For these measurements Au and In electrodes were evaporated on prismatic plane surface and electron beam with primary energy of 16–18 keV was used. EBIC technique gives the possibility to control free electron lifetime (τ_n) space distribution [5]. It is known that in high-resistivity CdS τ_n increases when Fermi level shifts toward c-band [6]. One can expect, therefore, that low-resistivity inclusions will manifest themselves as the regions of higher τ_n. These regions were seen at EBIC images as bright narrow lines 2–3 μm wide (Fig. 2). The density of these lines was found to coincide with the density of etch pits on (0 0 0 1) plane of the same sample.

US was excited in the crystals by means of ruby laser nanosecond pulse irradiation [7]. To avoid the possible effect of laser light on the sample characteristics irradiated surface was covered with copper foil [8]. The duration and intensity of excited US pulses were controlled over piezoelectric voltage (PV) that appeared in CdS crystal under US. A tandem of damped PV pulses with damping time 10^{-5} s was observed. At irradiation power density $P \approx 10^9\,W/cm^2$ the value of the first PV pulse was 2.5 V. Dislocation multiplication was not observed after US treatment, i.e. the case of $U < U_{th}$ took place.

Photocurrent (PC), thermally stimulated current (TSC) and photoluminescence spectra were measured under direct voltage in crystals with different N_D before and after US treatment. It was found that laser irradiation resulted in the drop of photocurrent (PC) (Fig. 3) and thermally stimulated current (TSC) (Fig. 4). The weakening of TSC peak at 40 K was essentially stronger than that of PC. It means that this peak value changed not only due to τ_n decrease, but also due to the decrease of the density of corresponding local centres in the crystal bulk [6]. It was shown earlier, that centres responsible for TSC peak at 40 K are

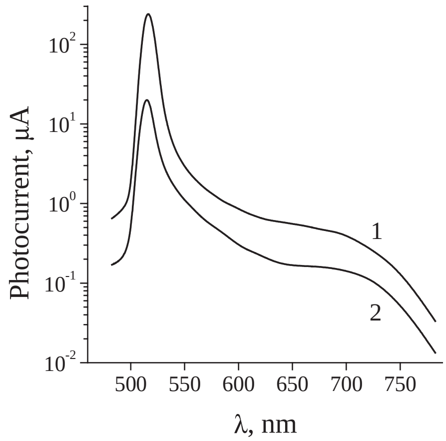

Fig. 3. Photocurrent (300 K) spectra of CdS crystal before (1) and after (2) pulse ultrasound treatment.

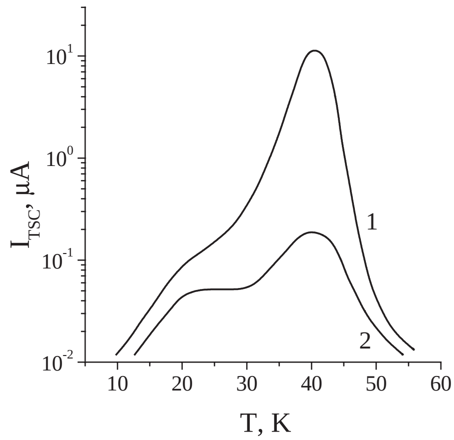

Fig. 4. TSC spectra of CdS crystal before (1) and after (2) pulse US treatment.

mobile shallow donors Cd_i [9]. The density of these donors in high-resistivity crystal bulk calculated from TSC curve [6] was 10^{15}–$10^{16}\,cm^{-3}$, which coincided with the value obtained from EPR measurements. PC and TSC changes were reversible: the initial characteristics restored after quick (1–2 min) annealing of the sample at 400 K or its holding at 300 K during 20–30 h (Fig. 5). The activation energy of restoration process evaluated from the temperature dependence of this process velocity was about 0.4 eV and coincided with Cd_i diffusion activation energy [9]. These results are in

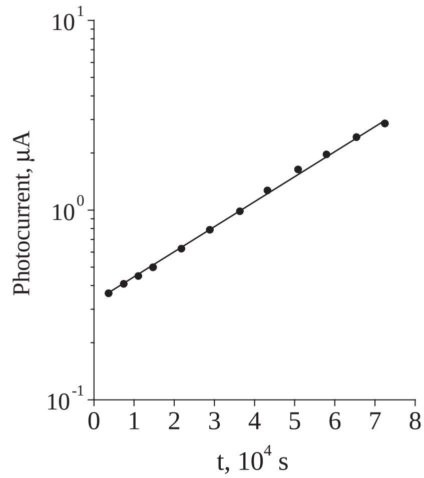

Fig. 5. Kinetics of photocurrent restoration process at 300 K after US treatment.

accordance with data reported in Refs. [1,3]. In addition to [1,3], the present investigations showed that US influence on crystal characteristics intensified with N_D. Besides, US action on the shape of edge green emission spectrum was found.

Green emission (GE) was excited by 365 nm line of 500 W mercury lamp at 77 K. This emission is known to be caused by radiative transition in donor–acceptor pairs and consist of zero-phonon band ($\lambda = 515\,nm$ at $T = 77\,K$) and its phonon replicas [10] (Fig. 6). It was found that the shape of GE spectrum depended on N_D: the more N_D, the greater the ratio I_1/I_0 of the intensity of the first phonon replica I_1 to the zero-phonon one I_0 (Table 1). After US treatment I_1/I_0 increased (Fig. 6). This increase was negligible in crystals with $N_D \leqslant 10^3\,cm^{-2}$ and maximum at $N_D = 10^6\,cm^{-2}$. The initial shape of GE spectrum restored simultaneously with restoration of PC and TSC spectra.

3. Discussion

It is known that the ratio of zero-phonon band intensity I_0 to that of phonon-assisted ones I_k is described theoretically by the expression:

$$I_k = I_0 N^k / k!, \qquad (1)$$

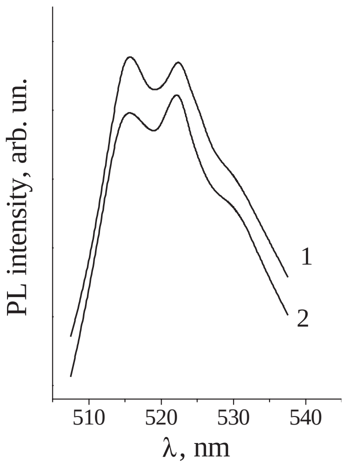

Fig. 6. Edge green emission spectra at 77 K before (1) and after (2) US treatment.

Table 1
Dependence of the ratio of zero-phonon line intensity to the first phonon replica intensity in green edge emission spectra (I_1/I_0) on dislocation density (N_D) in CdS crystals

N_D (cm^{-2})	I_1/I_0
10^2–10^3	0.8
10^4–10^5	0.9–1.1
5×10^5–10^6	1.2–1.3

where k is the number of phonon replica and N is electron–phonon interaction coefficient. The shape of GE spectrum in the most perfect CdS platelets corresponds to (1), the ratio I_1/I_0 being equal to 0.8 [10]. At the same time "distorted" GE spectrum with $I_1/I_0 \geqslant 1$ is often observed in CdS crystals, especially, bulk ones [11]. For as grown crystals such spectrum distortion was proved to be caused by reabsorption of emitted light due to the shift of absorption edge to the long-wavelength side [11,12]. It was shown that the value of this shift increased with shallow donor density n_d. The appearance of absorption "tail" at high n_d value was accounted for by formation of c-band state density "tail" and by optical transition to that from v-band [11]. In high-resistivity crystals with distorted GE spectrum low-resistivity inclusions were found and correlation between the density of such inclusions and the value of absorption edge shift was established [11,12].

The results of EPR and EBIC investigations showed that: (i) investigated crystals contained low-resistivity regions with high shallow donor density ($n_d \geqslant 10^{17}\,cm^{-3}$); (ii) these regions looked like narrow straight lines; (iii) the density of these lines coincided with N_D. One can conclude, therefore, that low-resistivity regions in as grown bulk CdS crystals are dislocations decorated with shallow donors. According to [11,12], the increase of I_1/I_0 testifies that under US treatment the density of shallow donors near dislocations increases. This state, however, is nonequilibrium, and equilibrium donor density restores with time due to diffusion of "superfluous" donors to the crystal bulk. The fact that the activation energy of restoration process coincides with that of Cd_i diffusion supports this conclusion. Thus, obtained results combined with analysis of earlier data testify that observed drop of n_d in crystal bulk under US is really due to gathering of shallow donors by dislocations.

Above results show also that study of GE spectrum shape can give the information about the density of dislocations and the extent of their decoration with shallow donors. This information can be useful in investigation of degradation of working elements of high-power electron beam-pumped CdS lasers (laser screens—LSs). The emission of LSs was observed to decrease in intensity and shift to long wavelength side during working process [13]. This effect is usually ascribed to the multiplication of dislocations that are considered as centres of nonradiative recombination [13]. Our measurements showed that degradation process was accompanied by considerable distortion of GE spectrum shape [12] (Fig. 7). So, one can conclude that LSs degradation is caused not only by creation of new dislocations but also by their decoration with shallow donors.

4. Conclusion

The influence of pulsed US on photoelectric and luminescent characteristics of CdS crystals has been investigated. The drop of shallow donor density in crystal bulk has been proved to occur under US. This result is in accordance with [3],

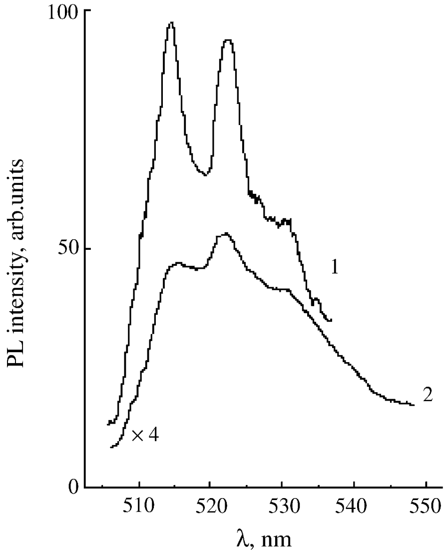

Fig. 7. Edge emission spectra of CdS laser screens before (1) and after (2) emitting of 10^5 pulses.

where sinusoidal US was used. It was supposed in Ref. [3] that observed effect resulted from gettering of shallow donors Cd_i by dislocations. The present investigations of EPR spectra and EBIC images, as well as of US influence on edge green emission spectrum shape give following arguments for this dislocation model:

- investigated crystals contain dislocations decorated with shallow donors;
- the intensity of US influence on crystal characteristics increases with dislocation density;
- the increase of the density of shallow donors near dislocations occurs side-by-side with its decrease in crystal bulk.

It has been shown also that the gettering of shallow donors by dislocations is one of the mechanisms of electron-beam-pumped laser degradation.

References

[1] S. Ostapenko, N.E. Korsunskaya, M.K. Sheinkman, in: S. Pizzini (Ed.), Defect Interaction and Clustering in Semiconductors: Ultrasound Stimulated Defect Reactions in Semiconductors, Scitec Publications Ltd, Switzerland, 2002, p. 317.

[2] I.V. Ostrovsky, V.N. Lysenko, Fiz. Tverd. Tela 24 (1981) 1206.

[3] A.P. Zdebsky, N.V. Mironyuk, S.S. Ostapenko, A.U. Savchuk, M.K. Sheinkman, Fiz. Tekhn. Poluprovodnikov 20 (1986) 1167;
A.P. Zdebsky, N.V. Mironyuk, S.S. Ostapenko, A.U. Savchuk, M.K. Sheinkman, Fiz. Tekhn. Poluprovodnikov 20 (1986) 1861.

[4] N.P. Baran, B.R. Dzhumaev, N.E. Korsunskaya, I.V. Markevich, L.Yu. Khomenkova, E.P. Shulga, Fiz. Tverd. Tela 38 (1996) 1735.

[5] M. Wada, J. Suzuki, H. Hogumatsu, Jpn J. Appl. Phys. 25 (Part 2) (1986) 780.

[6] V.E. Lashkarev, A.V. Lubchenko, M.K. Sheinkman, in: Nonequilibrium Processes in Semiconductors, Naukova dumka, Kiev, 1981.

[7] V.A. Yanushkevich, Phys. Chem. Treated Mater. 7 (1975) 9.

[8] A.N. Annanniyasov, Y. Garyagdyev, B.R. Dzhymaev, A.P. Zdebsky, N.E. Korsunskaya, I.V. Markevich, M.K. Sheinkman, Ukr. Phys. Zhurn. 34 (1989) 1251.

[9] N.E. Korsunskaya, I.V. Markevich, T.V. Torchinskaya, M.K. Sheinkman, J. Phys. C 13 (1980) 1275.

[10] M. Aven, J.S. Prener (Eds.), Physics and Chemistry of II–VI Compounds, North-Holland, Amsterdam, 1967, 624pp.

[11] L.V. Borkovskaya, B.R. Dzhymaev, N.E. Korsunskaya, I.V. Markevich, A.F. Singaevskiy, Sov. Phys. Semicond. 30 (1996) 745.

[12] L.V. Borkovska, Role of Macrodefects in Electronic and Ionic Processes in Crystals and Epitaxial Layers of II–VI Compounds, Ph.D. Thesis, Kyiv, 1999.

[13] A.S. Nasibov, L.N. Pechenov, V.I. Reshetov, Trydi FIAN 202 (1991) 68.