Conference paper

OPTO-ELECTRONICS REVIEW 7(2), 139–143 (1999)

Degradation processes in II–VI-compounds-based electron-beam-pumped lasers and creation of material with uniquely high optical strength*

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The processes of gradual degradation as well as the destruction processes of high power electron beam pumped lasers have been studied. The main reason of gradual degradation has been shown to be the increase in dislocation density due to thermoelastic stresses caused by both electron beam treatment and own laser radiation. The types of macrodefects that are responsible for laser screen destruction have been identified. CdS crystals obtained by the method developed by us were shown to have the highest optical strength.

Keywords: II-VI compounds, electron-beam-pumped lasers, degradation

1. Introduction

Electron-beam-pumped lasers are among the most attractive light-emitting devices of new generation that show promise for high quality TV projectors, air navigation, etc. Working elements (so-called, laser screens – LSs) of such visible-emitting lasers are usually made from II–VI compound semiconductors both single-crystalline and quantum-confinement. Degradation of such working elements is one of the main obstacles to the wide use of lasers. Such a degradation is most essential at high radiation power or in those cases where the quantum-confinement structures are used as working elements. Degradation processes of electron-beam-pumped lasers have been studied previously [1–3] except for the high-power lasers that work at high excitation levels (say, at electron energy about 200 keV and current densities from 20 to 40 A/cm^2).

In this work the degradation processes of single-crystalline CdS LSs of a pulsed electron-beam-pumped laser have been studied at a pulsed emitting power of about 4 MW and pulse duration 20 ns.

2. Experiment

Both bulk CdS single crystals and LSs fabricated from those crystals have been investigated. The crystals studied had been grown from the vapour phase either at a controlled ratio of pressures of sulphur and cadmium sulphide vapours $\alpha = P_S/P_{CdS}$ (at $\alpha = 0.5$ to 2.5) [4], or by a new method developed by us previously [5]. A common employed method for fabricating the LSs has been used [2]. The thickness of crystals that form a part of LS was 150 to 200 μm. Crystal generation was excited at electron beam energy 200 keV, pulse duration 20 ns, pulse frequency 1 Hz, the crystal temperature was about 77 K. The dependence of radiation intensity on the number of emitted pulses as well as the transformation of radiation spectra in the course of LS degradation was also studied. In addition, the dislocation densities were measured by an X-ray method at different stages of degradation. The surface of LSs after emitting 10^5 pulses at a pulse power from 2 to 4 MW was examined by means of a metallographic microscope.

To establish the mechanism of LS degradation, effect of different factors on the characteristics of CdS crystals used to fabricate the LSs, has been studied. Among those factors are the following:

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* The paper presented there appears in SPIE Proceedings Vol. 3724, pp. 244–248.

(i) the crystal heating by the electron beam;
(ii) nonthermal effect of nonequilibrium carriers generated by electron beam;
(iii) laser emission of the LS.

Taking those factors in mind, we have studied the effect of following crystal treatments on the spectra of photoluminescence, photoconductivity and optical transmission of the crystals:

(i) short-term (Δt = 1 to 3 min) heating of crystals up to T = 150 – 200°C;
(ii) irradiation by the scanning electron beam (E = 75 keV, I = 70 A/cm^2) in the TV scanning regime;
(iii) laser beam irradiation at quantum energies lower than the band gap width of cadmium sulphide ($h\nu < E_g$).

A ruby laser with a pulse duration 20 ns and power density from 1 to 100 MW/cm^2 was used as an irradiation source. The threshold power density for optical destruction of crystals studied were determined by the one-pulsed method developed by us previously [6]. Photoluminescence and photoconductivity were measured at 77 K; photoluminescence was excited by the 365 nm line of the mercury lamp. In addition densities of dislocations and of Cd inclusions were measured by the selective etching method both before and after the crystal treatment.

3. Results and discussion

Figure 1(a) shows the dependencies of generation intensity (I) of LSs on number N of pulses emitted. The measurements were made on the laser screen LS1 fabricated from the CdS crystal grown from the vapor phase under the excess sulphur pressure α = 2.1 (curve 1) and on the laser screen LS2 fabricated from the CdS crystal grown by the method developed by us (curve 2). As it can be seen, the behaviour of I (N) curves depends on the method of crystal preparation. Indeed, for the LS1 laser screen (curve 1) the generation intensity is independent of N up to 10^4 (portion I), then the intensity slowly decreases (portion II) and, at a dose 2×10^5 pulses, generation disappears (point III). It was found that point III is shifted to the side of lager N with increasing α at $\alpha < 1.6$, and is shifted to the side of smaller N with increasing α at $\alpha > 1.6$. The dependence similar to the above portion II only is observed for the LS fabricated from the CdS crystal grown by the method described in [5] [Fig. 1(a), curve 2]. Decrease in the laser intensity over the section II is accompanied by the shift of a generation spectrum to longer wavelength side [Fig. 1(b)].

Investigations of that side of the LS that is irradiated by electrons have shown that no visible changes occur prior to point III but just in the point III the destruction of the crystal surface takes place, that is the reason of LS destruction. And, that is important, the destructions of the mirror and the crystal surface below this mirror have the similar view.

3.1. Study of the gradual degradation

As the measurements of the etched pits density have shown, the densities of dislocations in the crystals used for fabricating LS1 and LS2 LSs were 5×10^4 and (3 to 5)$\times10^2$ cm^{-2}, respectively. It has been also shown for LS1 that the value of γ is practically unchanged over the section I and rises significantly over the section II. At the same time the increase in γ has

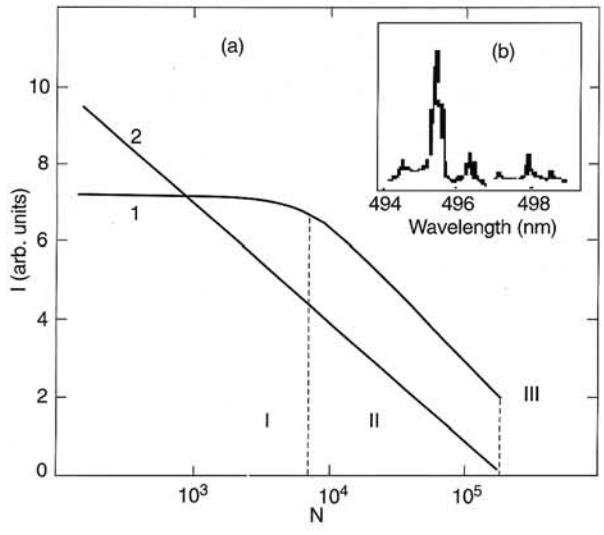

Fig. 1. Dependence of generation intensities of LSs on pulse number (a), shift of generation band (b).

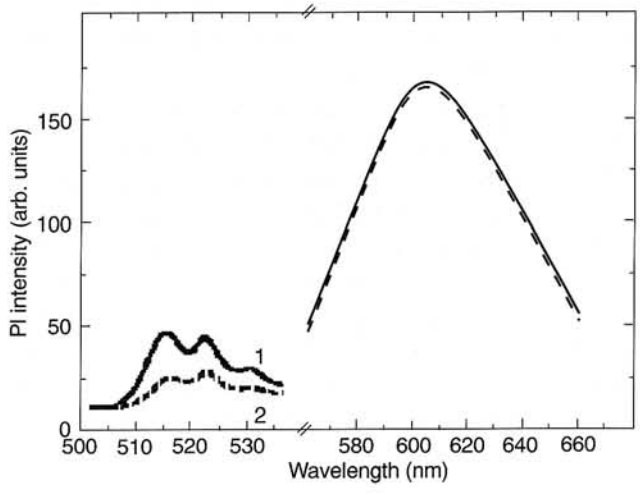

Fig. 2. Photoluminescence spectra of CdS crystals before (1) and after (2) heating.

been observed over the whole period of degradation of LS2. After emitting 10^5 pulses, the density of dislocation was approximately the same for both types of LSs and equals about 5×10^6 cm^{-2}. This makes it possible to suppose that the decrease in generation intensity is connected with the increase in dislocation density and the value of such a decrease is determined by the relative change of γ. Indeed, the value of I is not changed as long as the density of newly formed dislocations $\Delta\gamma$ is smaller than the initial value of γ, but the generation intensity begins to fall as soon as $\Delta\gamma$ begins to exceed γ. This mechanism of degradation is different from that for the electron-beam-pumped lasers with smaller power whose degradation, in accordance with [1–3], is mainly due to formation of Cd precipitates.

3.1.1. Effect of heat treatment on crystal characteristics

We showed that the short-term heat treatment of CdS crystals up to 150–200°C often results in the increase in dislocation density, probably due to residual strain relaxation. Such an increase is accompanied by the significant changes in the optical, luminescent and photoelectrical characteristics of the crystals. As it can be seen in Fig. 2, after such a heating, the intensity of the "orange" band at λ = 620 nm is not practically changed but the intensity of the "green" edge band (whose zero-phonon line is situated at 515 nm) is significantly lower. The crystal photoconductivity is also decreased.

Such a prevailing decrease in the "green" band intensity is indicative of the decrease in the respective recombination centers ("green" g-centers) in the crystal value. Because g-centers are responsible for the photosensitivity of CdS crystal at 77 K, their partial disappearance may be one of the reasons for the photocurrent decreases. Probably, g-centers "disappear" partially with increasing γ because of decoration of newly formed dislocations by such centers. A similar process has been already described previously [7].

The decrease in green band intensity is accompanied by the change in the band shape. Indeed, before heating, the intensity of the zero-phonon line exceeds the intensities of the phonon lines but, after the heating, the 1st phonon line is higher than the zero-phonon line. As it was shown previously [8], such a change in the shape of the "green" band is due to absorption of the luminescence radiation by the crystal and results from the presents of the long-wavelength tail (0.50–0.53 nm) in the vicinity of the fundamental absorption edge. This tail is connected with decorated dislocations [8]. Thus, the increase in dislocation density and decoration of dislocations by the g-centers result in the decrease in density of non-equilibrium electrons and in the rise of light absorption (and/or scatter) in the vicinity of fundamental absorption edge. This latter result is confirmed by the optical transmission spectra measured before and after crystal heating.

Because generation occurs at high excitation levels, the decrease in the g-center density in the crystal value has no significant effect on the density of non-equilibrium electrons and, hence, on the generation intensity. At the same time, the decrease in optical transmission in the vicinity of the fundamental absorption edge may result in the fall of generation intensity as well as in the shift of generation band into the long-wavelengths side. Just this effect has been observed experimentally [Fig. 1(b)]. Note that the decrease in generation intensity may be also connected with the increasing recombination velocity in the vicinity of dislocations [1–3]. The effect of heat treatment on the value of γ described above makes it possible to conclude that crystal heating by the electron beam is one of the reasons for the rise of dislocation density.

3.1.2. Effect of pre-threshold laser irradiation on crystal characteristics

The decrease and the change in the shape of luminescent "green" band described above have been also observed after laser irradiation of crystals at power densities lower than the threshold for optical destruction of crystals. Thus, the laser emission of the LSs results in the increase in γ as well which is due to absorption of this emission by the macrodefects and by their heating (see below).

3.1.3. Effect of irradiation by the electron beam on crystal characteristics

The crystal irradiation by the electron beam results in the dominating decrease in the green band but its shape remains unchanged. Concurrently, a conductive layer appears near the crystal surface. This layer manifests itself in the appearance of storage conductivity [9] and is a result of excess cadmium appearance due to crystal radiolysis [1–3]. The reason of a drop of green band intensity is the g-center density decrease apparently due to radiolysis process.

Due to the fact that the shape of the green band is not changed after electron beam irradiation of the crystal, it may be supposed that the density of dislocations remains practically unchanged. Because radiolysis is slow if the crystal surface is covered by a mirror [3], than, its effect on the LS characteristics cannot be essentially apparent.

3.2. Study of LS destruction

Principally, destruction of LS surface may be connected both with the influence of the electron beam and of the LS emission. As it is found in this work, the number N_R of pulses emitted by the LS before its destruction depends on the method for crystal grow, and, in particular, on the relative pressures of components (S and Cd) in the vapour phase from which the crystal is grown. This dependence is as follows; N_R initially increases and than decreases with increasing α.

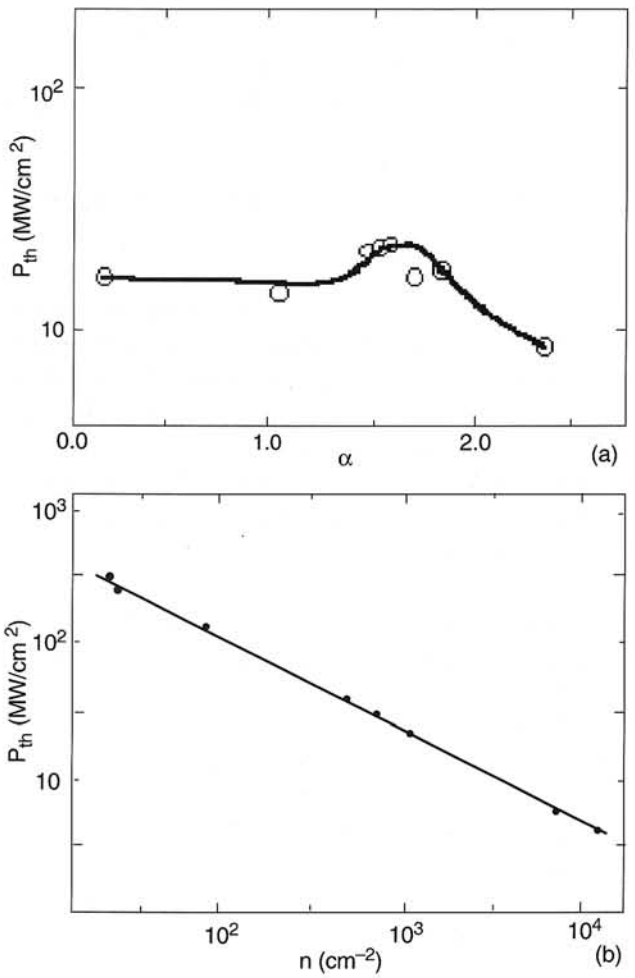

Fig. 3. Dependence of the threshold of optical destruction of CdS single crystals upon the relation of S and CdS vapour pressures, α (a) and Cd inclusions density (b).

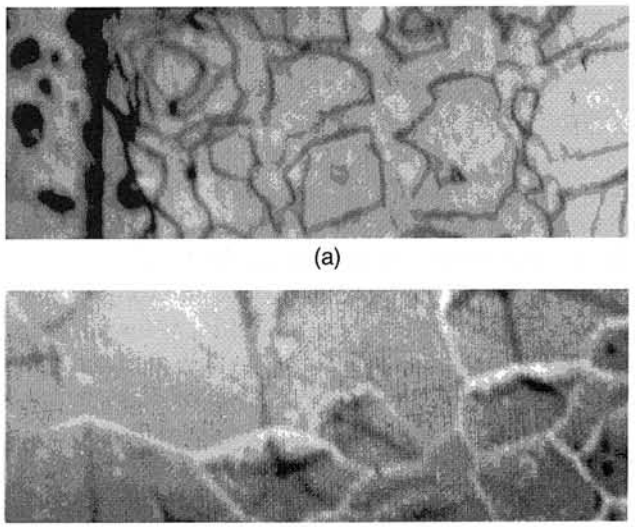

Fig. 4. Plan view of LS destruction surface after 10^5 pulse radiation (a) and initial crystal structure (b).

The similar dependence was also observed for the threshold P_{th} for optical destruction of the crystals; the dependence $P_{th}(\alpha)$ has its maximum at $\alpha = 1.6$ [Fig. 3(a)]. Correlation between the dependencies $P_{th}(\alpha)$ and $N_R(\alpha)$ indicate that the LS destruction is due to crystal erosion by its own radiation. This supposition is supported by a correlation between the types of destruction of a LS surface and of the corresponding crystal. Indeed, such a destruction manifests itself as randomly positioned spots of different shape both for the crystals grown at $\alpha < 1.6$ and for LSs fabricated from those crystals. If $\alpha > 1.6$, the destruction manifests itself as an irregularly shaped network (Fig. 4).

Note that the density of radiation of LSs is lower than the values P_{th} noted above. This is due to the fact that the values of P_{th} were determined by the one-pulsed method while the LS had emitted about 10^5 pulses, i.e., the lower values of P_{th} for LSs are due to the well-known effect of storage [10].

Taking in mind that the optical destruction of the transparent materials is usually initiated by the light absorption by macrodefects and by their heating, we have also examined the type and the density of such macrodefects in the crystals grown at different α. Three types of macrodefects have been observed; those are: dislocations, Cd inclusions, and boundaries of the adjacent crystals (for block crystals). At $\alpha < 1.6$, we have observed Cd inclusions about 20 μm in size as well as dislocations but the intercrystalline boundaries were absent. The density of inclusions fell with increasing and inclusions were not detected at $\alpha > 1.6$. So, at $\alpha > 1.6$ we have observed dislocations and intercrystalline boundaries whose density in-

creased with increasing α. The dislocation density was practically the same over the whole range of α under investigation.

It was found that the threshold for optical destruction had decreased with increasing inclusions density in those crystals that were grown at $\alpha < 1.6$ and had the Cd inclusions similar in size [Fig. 3(b)]. Thus, the destruction of such crystals was due to absorption of laser emission by such inclusion. This supposition was supported by the view of destructions. At the same time, for the crystals grown at $\alpha > 1.6$, the threshold value sharply fell with increasing intercrystalline boundaries density and destructions manifested themselves as crystal cracking along such boundaries (Fig. 4). Hence, it can be seen that dislocations have no essential effect on the processes of optical destruction.

Thus, the highest optical strength on the crystals grown at $\alpha = 1.6$ and the maximum service life of the relative lasers screens [2] are due to the low density of Cd inclusions and to absence of intercrystalline boundaries. Hence, to increase the service life of LS, one must develop a method for crystal growing that makes it possible to grow the single crystals with a low density of Cd inclusions and without the intercrystalline boundaries.

The crystals grown by the technology developed in Ref. 5 just meet those requirements. Those crystals have no intercrystalline boundaries, the density of inclusion is about 10 cm^{-2}, the value of P_{th} is about one order of magnitude higher than in crystals grown at $\alpha = 1.6$. LSs fabricated from such CdS crystals have no visible destructions even under those conditions where the LSs made from other CdS crystals are cracked. It can be shown that the presence of Cd inclusions and intercrystalline boundaries with concentrations depending on crystal growth conditions is the reason of LSs destruction.

4. Conlusion

The gradual degradation of LSs studied is the result of the increase in dislocation density due to thermoelastic stress caused by both the effects of the electron beam irradiation and the laser generation emitted by the LS. This conclusion agrees with the mechanism proposed for the high power lasers previously [1]. At the same time, the LS destruction is shown to be due to the laser generation emitted by the LS.

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