Defect annealing in a II–VI laser diode structure under intense optical excitation

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Defect annealing under intense pulsed optical excitation has been observed in a II–VI laser diode structure at room temperature. More than one order of magnitude increase in photoluminescence intensity has been obtained when the annealed area is probed at low excitation intensity. High-resolution confocal photoluminescence images of the annealed region do not show any sign of degradation. Together, these results suggest that an initial density of intrinsic point defects present within the active region can be removed by the optical annealing. Recombination-enhanced defect reactions in the vicinity of the point defects are responsible for this nonthermal annealing effect. © *1998 American Institute of Physics.* [S0003-6951(98)00502-6]

Macroscopic defects originating at the GaAs/ZnSe heterointerface such as stacking faults and threading dislocations have been recognized to be the main cause of the rapid degradation and, therefore, the very short operating lifetime of II–VI-based laser diodes.[1–4] Considerable effort has been put into reducing the stacking fault density to less than the critical value of 10^4 cm^{-2} in order to obtain a laser diode with no extended defects in its stripe area (typically, 10 μm$\times$600 μm). At present, a 100 h lifetime continuous-wave laser diode operating at room temperature has been achieved with a stacking fault density lower than 3×10^3 cm^{-2}.[5] For further improvement, slower degradation mechanisms, such as point defect diffusion and reaction, need better understanding.

It has been shown recently that recombination-enhanced defect reaction (REDR) is the driving force of the degradation in relatively long-lived II–VI light-emitting diodes.[6] Recombination-enhanced processes in semiconductors have been thoroughly studied over the years.[7–9] REDR describes how the energy released by nonradiative carrier trapping at point defect sites can excite localized vibrational modes of the defect and of the surrounding atoms, before being dissipated through lattice phonons. This energy can be used to promote defect motion and reaction, inducing defect multiplication (degradation), or, alternatively, defect reduction (annealing).

In this letter we report an improvement in photoluminescence (PL) efficiency in a II–VI laser diode structure using high intensity laser excitation. Instead of observing degradation, we find that the PL efficiency increases as a function of time through optical annealing of the II–VI material. PL maps of the annealed area were also performed using a confocal microscope[10] setup (0.5 μm resolution) and show that no degradation occurred in the active region during the annealing process.

The sample studied was a ZnCdSe/ZnSSe/ZnMgSSe single quantum well separate-confinement heterostructure (SCH) grown by molecular beam epitaxy (MBE). The SCH structure is similar to the laser structure reported before,[5] except that a part of the p-type layer has been removed by chemical etching to allow optical pumping to be performed.

The sample was annealed at room temperature by optical excitation using a synchronously pumped mode-locked dye laser operating at 440 nm and providing 5 ps pulses at a repetition rate of 76 MHz. We term this the ‘‘pump’’ beam for our studies. An excitation spot was formed at the quantum well by displacing the stationary sample axially from the focal plane of the objective lens. The excited region was then probed using the 458 nm line of a continuous-wave (cw) Ar-ion laser. We term this the ‘‘probe’’ beam. We used the Ar-ion laser for the probe PL measurements due to its superior signal-to-noise ratio. Both pulsed and cw beams are spatially overlapped to probe exactly the pumped spot. The PL was dispersed by a 1 m spectrometer and imaged onto a optical multichannel analyzer camera. PL confocal imaging was achieved by placing the quantum well in the focal plane of the 0.6 NA (numerical aperture) objective lens, raster scanning the sample in the plane of growth, and imaging the PL through a pinhole in the detection plane.[11]

Figure 1(a) shows a 160$\times$160 μm size PL image (observed with the probe) taken after exciting a spot of about 120 μm diameter with 350 W/cm^2 (pump beam) for 90 min. One can see the absence of dark spot defects and the subsequent $\langle 100\rangle$ dark line defects which are usually observed and have previously been recognized as the principal cause for the rapid degradation of the active layer in II–VI laser diodes.[1–4] Instead of this, an increase in PL efficiency can be observed in the area previously submitted to intense optical excitation. As a comparison, Fig. 1(b) shows an image taken after exposing a similar laser structure with much larger stacking fault density to the same excitation conditions for 9 min. In this case, fast growing dark spots and rapidly propagating dark lines can be observed within the active region, causing a dramatic decrease in PL efficiency. Annealing of

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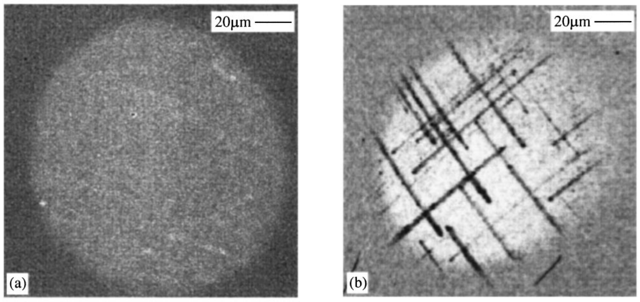

FIG. 1. 160×160 μm PL micrographs of two ZnCdSe/ZnSSe/ZnMgSSe laser structures taken after exciting a spot of about 120 μm diameter with an average power density of 350 W/cm^2 for (a): 90 min; and (b): 9 min.

the nondegraded areas inside the excited spot can also be observed.

We believe that this increase in PL efficiency is an intrinsic property of the II–VI material and that it is similar to the recombination-enhanced defect annealing phenomenon observed during aging studies in III–V laser diodes grown by MBE and by metalorganic chemical vapor deposition.[12] High electrical injection in these devices can enhance point defect diffusion, hence rearranging their position in such a way as to decrease their density. As point defects also act as nonradiative centers of recombination, the annealing process will result in an increase in PL efficiency. The absence of dark line defects for the sample in Fig. 1(a) allows a definite conclusion of REDR as the annealing mechanism. The presence of such defects for the sample in Fig. 1(b) makes the interpretation of the annealing mechanism much more difficult.

In order to quantify this increase in PL efficiency, we carried out the following steps: (I) We excite with the picosecond dye laser (440 nm) with an average pump excitation intensity of 1 kW/cm^2. (II) We switch off the picosecond laser and probe the annealed spot with a cw Ar-ion laser (458 nm) at a probe intensity of 50 W/cm^2. Stages I and II are then repeated. The 20 μm diameter spot was annealed for 60 min. Figure 2 shows the gradual increase in PL intensity as a function of annealing time. We see that during the time frame of our measurements an increase in PL intensity of greater than a factor of 4 was obtained and no saturation of the annealing process occurred. In addition, no spectral shift or broadening of the PL spectra was observed.

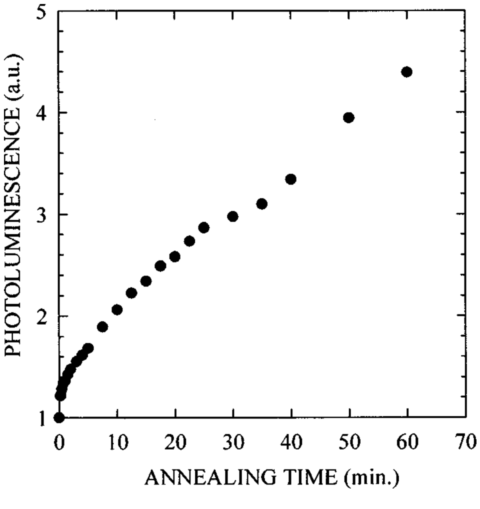

FIG. 2. PL increase as a function of annealing time of 20 μm diameter spot annealed for 60 min at an average pump excitation intensity of 1 kW/cm^2. The excitation intensity for the probe was 50 W/cm^2.

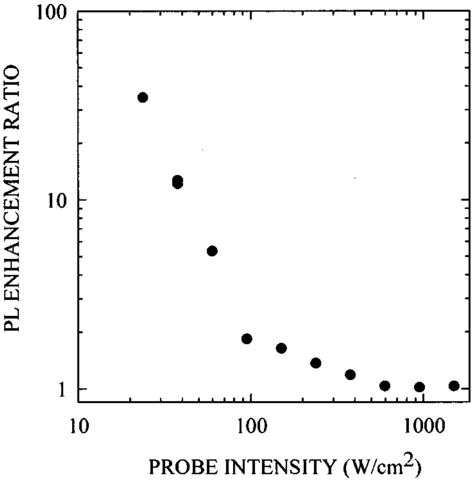

FIG. 3. PL enhancement factor (ratio of the PL intensity inside and outside the annealed spot) measured after 60 min of annealing as a function of probe intensity.

After annealing, a confocal micrograph of the annealed region was taken. No dark spots/lines were formed during the annealing process. More careful inspection inside and just around the spot using a 0.9 NA objective lens did not show any evidence for agglomeration of point defects into clusters. Such clusters were first recognized by Haugen *et al.*[13] and usually emanate from macroscopic defects present in the active region.

The increase in PL efficiency is only relative and depends on the excitation intensity of the probe Ar-ion laser. In Fig. 3 we plot the PL enhancement ratio, defined as the ratio of the PL inside and outside the previously annealed spot, as a function of probe excitation intensity. We can see that at low probe excitation ($\sim$20 W/cm^2) the PL enhancement ratio is more than 30 and that it gradually decreases with increasing excitation to become negligible at high excitation intensities (0.5–1.5 kW/cm^2). This behavior is a direct consequence of the saturation of nonradiative centers of recombination with increasing carrier densities. We see that annealing reduces the density of point defects but that we are only sensitive to this effect at low probe excitation intensity.

It is clear that, in our case, the annealing behavior is not due to global heating of the lattice as we observe a redshift of only 11 meV between the PL excited with the pump beam (1 kW/cm^2) and the PL excited with the probe (50 W/cm^2). Assuming that the band-gap shrinkage is only caused by lattice heating, the shift would suggest a temperature rise of about 15 °C,[14] which is well below the growth temperature of II–VI materials. On the other hand, we found that carrier recombination is required for annealing to occur because pumping below the band with a 532 nm laser beam is found to be ineffective in annealing the material.

The work of Watkins indicates that interstitial Zn_i is mobile at room temperature while its Frenkel pair, the Zn vacancy V_{Zn} is stable.[15] Carrier recombination may further increase the mobility of the interstitial or may allow for vacancy migration. Alternatively, both of the above processes could occur. Further studies are required to elucidate which defects are mobile and which defect reactions occur in these II–VI semiconductors.

In conclusion, optical annealing by intense pulsed laser treatment has been observed in a II–VI laser structure. A corresponding increase in PL efficiency was measured as a function of probe excitation intensity and shows that the PL enhancement depends on the probe excitation intensity and can exceed one order of magnitude at low excitation. High-resolution PL images of the annealed region were also performed and do not show any evidence of dark defect generation and degradation in the best material. We believe that carrier recombination-induced annealing is an intrinsic property of the ZnCdSe-based laser diode material and that it is an important step forward in the development of II–VI semiconductor materials.

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