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# Characterization of ZnMgSSe-Based Wide-Gap Laser Diodes

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Device lifetime exceeding 100 hours has been achieved for a ZnCdSe/ZnSSe/ZnMgSSe separate-confinement heterostructure laser diode under room-temperature continuous-wave operation. This long lifetime has been realized by reducing the density of pre-existing defects which are nucleation sources for the formation of degradation defects. The failure of this laser diode is attributed to gradual degradation caused by point defects, not by extended defects. Time-resolved photoluminescence spectroscopy was employed to study the nonradiative recombination centers in the quantum well.

## 1. INTRODUCTION

Blue and green light-emitting devices have been studied intensively to realize outdoor full-color devices and the next generation of high-density optical recording systems. With successful *p*-type doping of ZnSe with nitrogen, Haase *et al.* demonstrated the first II-VI laser diodes (LDs) at 77 K.[1] Since then, laser diodes based on II-VI semiconductors have been further developed. Incorporating Mg in Zn- and Cd-chalcogenides[2] opens up a wide range of II-VI materials having both a wide bandgap and a large lattice constant. ZnMgSSe compounds have made room-temperature (RT) continuous-wave (CW) operation possible and the device characteristics of II-VI LDs, such as high power operation and low threshold current, are equivalent to those of well-established III-V LDs.[3] A major target in research on II-VI LDs is the extension of the device lifetime, which is vital for commercial applications.

In this paper, we describe rapid degradation in ZnMgSSe-based light emitting diodes (LEDs) and report an LD that achieved a long lifetime due to reduced pre-existing defect density. Finally, we discuss point defects which limit the lifetime of devices without pre-existing stacking faults.

## 2. RAPID DEGRADATION

To clarify the cause of short device lifetime, we performed electroluminescence (EL) and transmission electron microscopy (TEM) observation of II-VI light emitters.[4,5] The epitaxial layers, including a ZnCdSe/ZnSSe/ZnMgSSe separate-confinement heterostructure (SCH), were grown by molecular beam epitaxy (MBE) on an *n*-GaAs (001) substrate. EL was imaged in an optical microscope through a transparent gold top contact.

EL microscopy shows that small dark spots are observed initially and become darker and spread out, forming a rough triangle in the <100> direction during operation. By comparing the EL and TEM images, the dark spots are found to correspond to stacking faults and the triangular dark regions are identified as networks of dislocations composed of dislocation dipoles and loops. The source of these highly dislocated regions is stacking faults which begin at the substrate/epilayer interface and are bounded by Frank partial dislocations with Burgers vector $\boldsymbol{b} = a/3\langle 111\rangle$. The dipoles themselves are closely aligned to the <110> directions lying in the {111} plane, with Burgers vector of the type $a/2\langle 011\rangle$ inclined at 45° to the (001) junction plane, as shown in Fig. 1.

The degraded region is thought to be formed as follows. Dangling bonds along dislocation cores are sites of nonradiative recombination. Local thermal stress, created by nonradiative recombination at the dislocation cores, assists, together with built-in stress, the dissociation formation of Frank partial dislocations into 60°-type perfect dislocation dipoles during current injection. After dissociation, dislocation networks expand by a combination of gliding, including cross-slip, and climbing, enhanced by nonradiative recombination of electron-hole pairs.

The results obtained here clearly indicate that the pre-existing stacking faults are the seeds of the highly dislocated regions which limit the lifetime of LDs, if they

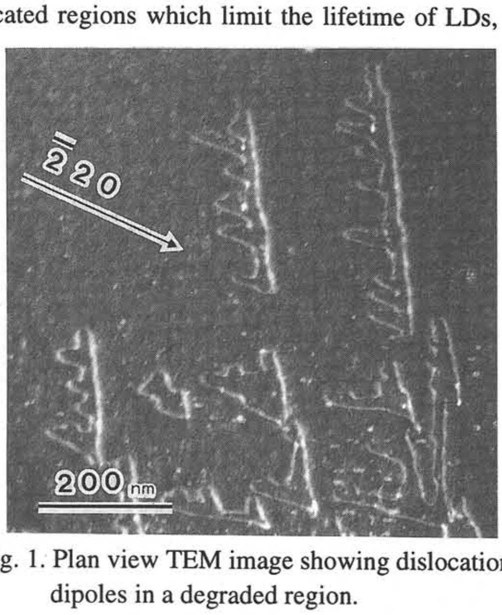


Fig. 1. Plan view TEM image showing dislocation dipoles in a degraded region.

have extended defects in their stripe areas. Therefore, it is necessary to reduce the crystal defects during growth to a density in which no dark spot exists in the stripe region.

## 3. LONG - LIVED LASER DIODES

One way to reduce stacking fault density is to use ZnSe substrates for homoepitaxial growth;[6] another way is to use a GaAs buffer layer.[7] We have achieved a dark spot density (DSD) of less than $3 \times 10^3$ cm$^{-2}$ by optimizing growth conditions of the II-VI/III-V interface.[8] After growing a GaAs:Si buffer layer on an $n$-type GaAs (001) substrate in a III-V chamber, the wafer is transferred to a II-VI chamber under ultra-high vacuum and the growth of II-VI layers is started after Zn beam exposure on the As-stabilized GaAs surface.

The epitaxial layers for the laser diodes consist of a GaAs:Si buffer layer, a ZnSe:Cl buffer layer, a ZnSSe:Cl buffer layer, a $Zn_{0.9}Mg_{0.1}S_{0.15}Se_{0.85}$:Cl cladding layer, a ZnSSe:Cl guiding layer, a $Zn_{0.65}Cd_{0.35}Se$ single quantum well (QW), a ZnSSe:N guiding layer, a $Zn_{0.9}Mg_{0.1}S_{0.15}Se_{0.85}$:N cladding layer, a ZnSSe:N layer, a ZnSe:N layer, a ZnSe:N/ZnTe:N multiple quantum well, and a ZnTe:N contact layer.

The threshold current under CW operation is 32 mA, which corresponds to a threshold current density of 533 A/cm$^2$, for a laser diode with a stripe area of 600 μm x 10 μm and a 70/95 % high reflective coating. The threshold voltage is 11 V and the lasing wavelength is 514.7 nm. RT CW aging tests were performed under automatic power control at 1 mW, as shown in Fig. 2. The lifetime of the LD at an ambient temperature of 20 ℃ is 101.5 hours, which is the longest RT CW lifetime of any II-VI LD so far reported. Since the DSD is sufficiently low, we believe that failure of this LD is caused by degradation not owing to pre-existing defects but to point defects. To conclude that definitely, however, we need further degradation analysis.

## 4. POINT DEFECT ANALYSIS

Now we have entered into a stage where the device lifetime of II-VI LDs is limited by gradual degradation caused by point defects. Studies of point defects in II-VI epitaxial layers are therefore the key to further improvement. In this context, we have performed time-resolved photoluminescence (PL) experiments which provide useful information about nonradiative recombination processes.[9]

The sample examined in this work is an $n$-type $Zn_{1-x}Cd_xSe$/ZnSSe quantum well ($x = 0.3$, $L_z = 6$ nm, $n = 1.2 \times 10^{17}$ cm$^{-3}$) which is used as an active region in SCH laser structures. The confinement energy $\Delta E$ in the quantum well was 0.30 eV. The sample was optically excited by a 200-fs pulse of a frequency-doubled Ti:sapphire laser. The PL was detected by a two-dimensional streak camera. The experiments were carried out from 8 to 375 K.

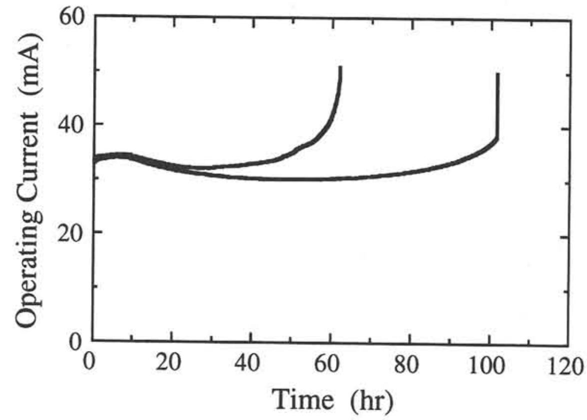


Fig. 2. Aging results under 1mW constant light output power at RT.

We consider recombination processes in a QW system with both excitons and free carriers, since excitons play a major role in the optical properties of QWs, especially at low temperatures, because of the large exciton binding energy and oscillator strength due to size quantization. We have described the theoretical model elsewhere.[9] Following this model, we can extract both the radiative and nonradiative recombination times ($\tau_r$, $\tau_{nr}$) as a function of temperature, as follows:

$$\tau_r(T) = \frac{I_0(8\text{ K})\,\tau(8\text{ K})}{I_0(T)\,\eta(8\text{ K})}, \tag{1}$$

$$\tau_{nr}(T) = \frac{1}{1/\tau(T) - 1/\tau_r(T)}, \tag{2}$$

where $\tau_r(T)$ is the radiative lifetime at temperature $T$, $\tau_{nr}(T)$ is the nonradiative lifetime, $\tau(T)$ is the PL decay time, $I_0(T)$ is the initial luminescence intensity, and $\eta(T)$ is the internal quantum efficiency. The data for $\tau_r$ and $\tau_{nr}$ are shown in Fig. 3. We get a decreasing $\tau_{nr}$ with increasing $T$, assuming $\eta(8\text{ K}) = 1$. Values for $\tau_{nr}$ for $T < 100$ K are ignored since they scatter due to the small contribution to $\tau$. If we assume that $\eta(8\text{ K})$ is less than unity, the values of $\tau_{nr}(T)$ are constant or increase with $T$, unlike the case for $\eta(8\text{ K}) = 1$, as shown in Fig. 3. This behavior is not expected, if we consider Schockley-Read nonradiative recombination or thermal emission out of the well. Hence $\eta(8\text{ K}) = 1$ is thought to be an appropriate assumption. If the thermal activation of carriers out of the well is the main nonradiative channel, the order of the activation energy should be comparable to the barrier height.[10-12] However, since the temperature dependence of $\tau_{nr}$ gives an activation energy $E_a$ of 11 meV, which is much smaller than $\Delta E$ , the thermal emission process from the well might not be the preferable decay channel in our II-VI well due to the large confinement energy. The nonradiative lifetime due to

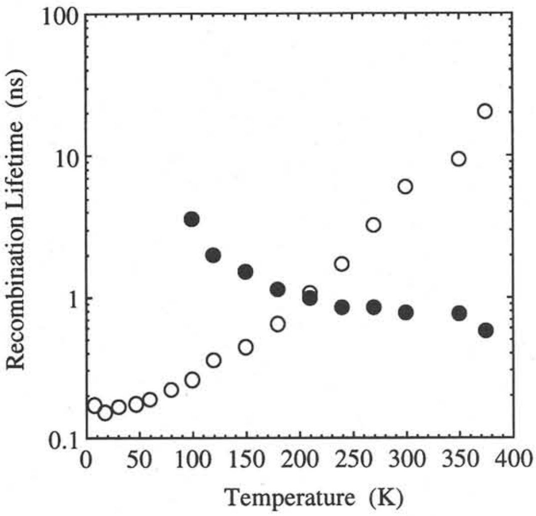


Fig. 3. Temperature dependence of $\tau_r$ (open circles) and $\tau_{nr}$ (closed circles) for $\eta$(8 K) = 1.

trapping at interface states can be written as

$$\tau_{nr}(T) = \frac{d}{2\sigma_\infty \exp(-E_a/kT)\, v_{th} N_s}, \tag{3}$$

where $d$ is the active layer thickness, $\sigma_\infty$ is the capture cross section at an infinite temperature, $E_a$ is the activation energy, $v_{th} = \sqrt{3kT/m^*}$ is the thermal velocity ( $m^*$ is the effective mass), and $N_s$ is the planar density of recombination centers. If nonradiative recombination occurs in the well, we expect the lifetime to vary as

$$\tau_{nr}(T) = \frac{1}{\sigma_\infty \exp(-E_a/kT)\, v_{th} N_T}, \tag{4}$$

where $N_T$ is the concentration of defect centers.

If we assume $\sigma_\infty$ of $10^{-14}$ cm$^2$, we can estimate $N_T$ and $N_s$ to be 1.4 x $10^{16}$ cm$^{-3}$ and 4.3 x $10^9$ cm$^{-2}$, respectively. From our data, we cannot determine if the process occurs in the bulk or at the interface. A detailed study of well thickness dependence will allow us to determine which nonradiative recombination mechanism applies. This thermally activated nonradiative recombination process reduces the luminescence quantum efficiency $\eta$ (= $\tau/\tau_r$) to 14 % at 300 K. This value of $\eta$ indicates that the quality of the active region of the II-VI laser can be further improved. As noted above, PL study is a useful technique to evaluate the changes in the point defect concentration, although it cannot reveal detailed microstructure of defects.

## 5. CONCLUSION

We have shown that the rapid degradation of II-VI light emitters is caused by pre-existing stacking faults originating at the II-VI/III-V interface. A lifetime of over 100 hours has been achieved at RT under CW operation for a ZnMgSSe-based LD with a DSD lower than 3 x $10^3$ cm$^{-2}$. We have entered into a stage where the operation of II-VI LDs is limited by point defects, not by extended defects. In order to establish the reliability of II-VI lasers, the density of point defects must be reduced.


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