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ADP012656

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Effect of Zn atom diffusion in the active layer of InGaAlP visible-LED investigated by the Piezoelectric Photothermal Spectroscopy

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ABSTRACT

It has been reported that Zn atoms diffused from the Zn-doped p-InAlP cladding to the active layer in InGaAlP visible-light-emitting diodes cause a degradation of light output efficiency. A doping effect of the Zn atoms was then investigated using a Piezoelectric Photothermal Spectroscopy from a nonradiative transition point of view. The results indicate that the Zn-doping unexpectedly induces a decrease of the nonradiative component of the electron transitions above the band gap of the active layer. The experimental results are explained by considering that Zn doping cause the increase of both shallow and deep acceptor levels at the same time with the different rate for generation.

INTRODUCTION

Recently, high-brightness operation from the orange to green region have been obtained for the InGaAlP LEDs using InAlP cladding layers and distributed Bragg reflectors (DBRs) grown by metal organic chemical-vapor deposition (MOCVD) method [1]. But one of the problems in the InGaAlP LEDs is a degradation of light output power, which may be caused by the presence of Zn atoms diffused from Zn-doped InAlP cladding layer during the device manufacturing processes. Since a lifetime of the injected carriers in the active layer decreased with increasing Zn concentrations, the diffused Zn was considered to create a not only shallow acceptor but also deep defect levels at the same time in the InGaAlP active layer [2]. However, details have not been clear yet.

For the semiconductors which have such deep levels, nonradiative processes may play an important role for the electron transition mechanisms. However, Photoluminescence methods can't detect such nonradiative transitions. The great advantage of the Piezoelectric Photothermal Spectroscopy (PPTS) is that it is a direct monitor of the nonradiative recombination processes of photoexcited electrons. Therefore, it is useful to clarify the effect of diffused Zn atoms in InGaAlP active layer from the nonradiative transition point of view. We have already reported [3, 4] that the nonradiative transition in semi-insulating bulk GaAs and in AlGaAs/GaAs heterostructure sample could be clearly understood by this technique. In this paper, we propose here a model for an effect of Zn doping and for an electron transition mechanism through the nonradiative pathways to explain our results. The effect of DBRs is

also taken into account. We conclude that deep defect level generated by the Zn atoms diffusion play an important role for the degradation of the LEDs.

EXPERIMENT

Two InGaAlP LEDs which have Zn-doped or not intentionally doped InGaAlP active layer were prepared to clarify an effect of Zn-doping. Figure 1 shows a schematic diagram of the present $In_{0.5}(Ga_{0.72}Al_{0.28})_{0.5}P$ LEDs samples. The $In_{0.5}(Ga_{0.72}Al_{0.28})_{0.5}P$ (hereafter, refer to InGaAlP) active, $In_{0.5}Al_{0.5}P$ (refer to InAlP) cladding and, DBRs layers were grown by MOCVD on (100) n-GaAs substrate tilted 15°off toward [011]. A DBR consisting of a pair of n- InAlP and n-GaAs is an important component to avoid a reduction of light extraction efficiency due to the light absorption in the GaAs substrate.

For the PPTS measurements, the piezoelectric transducer (PZT) was attached ton the GaAs substrate side of the sample using a silver conduction paste. The probing light from a grating monochromator was mechanically chopped and focused on the epitaxial layers side. Details of the experimental procedures were reported previously [5].
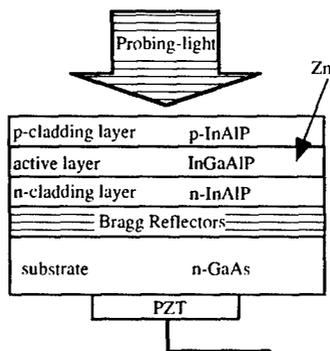
Figure 1. Schematic diagram of InGaAlP LEDs samples. For the PPTS measurements, the piezoelectric transducer (PZT) was attached to the GaAs substrate side of the sample using a silver conducting paste. The probing-light from a grating monochromator was mechanically chopped and focused on the epitaxial layers side.

RESULTS AND DISCUSSION

The PPT spectra of non- and Zn-doped InGaAlP LEDs at 297K are shown in Figure 2. For the non-doped sample, the PPT signal peaks that reflect well the optical properties of the n-GaAs substrate are observed below 1.4eV, which corresponds to the direct bandgap energy (E_g) of GaAs of 1.43eV at 297K. In the higher energy region, the PPT signals show a rapid increase and a subsequent decrease about 2.1eV and 2.6eV, respectively. These photon energies correspond to E_g of InGaAlP (2.07eV) and of InAlP (2.5eV) at 297K, respectively [6]. Therefore, it can be considered that the PPT signals ranging from 2.1eV to 2.6eV are due to the

nonradiative transition in the InGaAlP active layers.   We hereafter refer this band to B-band.
Figure 2 also shows the effect of Zn-doping in InGaAlP active layers.   The PPT signal intensity
of the Zn-doped sample decreases about 12 times smaller than that of non-doped one.   If
Zn-related levels induced by a doping act as a nonradiative recombination center, the PPT signal
intensity should increase.   This is not the case for the present result.

Additional fine structure is observed in the photon energy region between 1.5 and 2.0eV,
below the band-gap of InGaAlP active layer. These are shown in Figure 3 with expanded vertical
scale. We consider this signal results from DBRs.   The calculated results for the reflectivity due
to the presence of DBRs are shown in Fig.3 by open circles.   The experimental results for
Zn-doped sample were also shown in the figure. All of the photon energy positions for observed
humps and dips are well corresponded to the calculated results.   The same result is observed for
non-doped sample.   However, the PPT signal intensity of the Zn-doped sample is larger than
that of non-doped one in this photon energy region.   The doping effect of the PPT signal
intensity is reversed below and above 2.1eV.
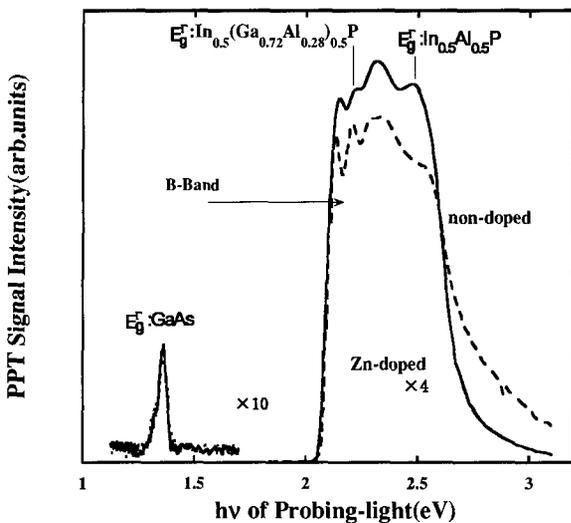
Figure 2.   PPT amplitude spectra of $In_{0.5}(Ga_{0.72}Al_{0.28})_{0.5}P$ at 297K.   The solid and broken curve
is non-doped and Zn-doped sample, respectively.
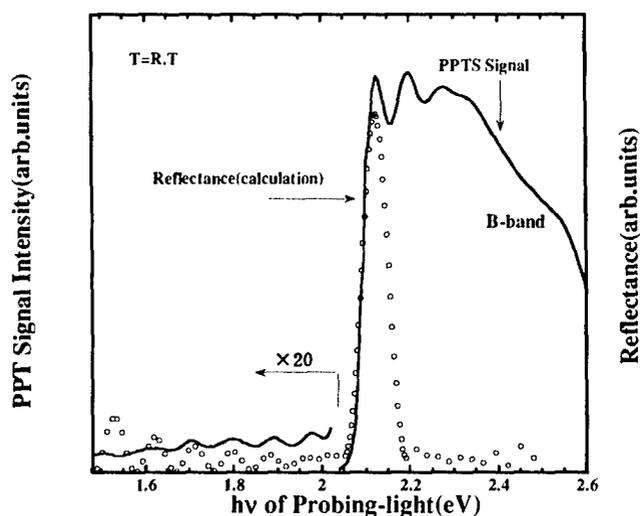
Figure 3. PPT amplitude spectra of Zn-doped sample and calculation of reflectance in DBRs at 297K. The solid curve and the open circle are experiment of Zn-doped sample and calculation of reflectance in DBRs, respectively. There is good agreement between experiment and calculation.

We, here, propose a carrier recombination model in the active layer for explaining why the PPT signal intensity of B-band decreases by doping. Supposing that the introduced Zn atom occupy the substitutional site in the active layer, it is reasonable to consider that the Zn atoms act as shallow acceptor levels even when the Zn atom resides at Ga or As site. We first propose that the transition of photo-excited electrons from conduction band to such shallow acceptor level generates the heat by the nonradiative process and cause the PPT signal. Since the Zn doping increases the concentration of those acceptor level, the PPT signal should increase with doping. However, this is not the case.

Then we consider next that the Zn atoms occupy the substitutional and the interstitial sites in the active layer. In this case, the Zn atoms form the shallow acceptor and the deep level, respectively, at the same time. The schematic model is shown in Figure 4. Transition (1) means excitation of electrons from valence to conduction band, transition (2) means radiative transition from conduction to valence band, transition (3) means radiative transition from conduction band to shallow acceptor level, transition (4) means nonradiative transition from conduction band to deep level and this cause the PPT signal. When the sample was doped with Zn atoms, the number of both shallow and deep acceptor levels increases. However, we further assume here that the increasing rate for the deeper acceptor level is small compared with that of shallow level. This is because that the Zn atom can easily reside at substitutional rather than at interstitial site. According to the present model, the number of photoexcited electrons that can recombine with

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the deep level and cause the PPT signal decreases with Zn doping. Most of the photoexcited carriers may recombine with shallow acceptor through the radiative transition and the number of the electrons that can recombine with deep level decreases. This results in the decrease of the PPT signal by doping.

Photoluminescence (PL) measurements for the same sample have already been carried out [2]. Since PL lifetime, determined from a time resolved PL technique, decreased by doping of Zn, they considered that introduced Zn atom from p-type clad to the active layer formed deep defect levels and caused the degradation for the luminescence. However, our model has assumed that the increasing rate for the deeper acceptor level was small than that of the shallow acceptor level. Detailed discussion for clarifying this inconsistency is now carrying on.
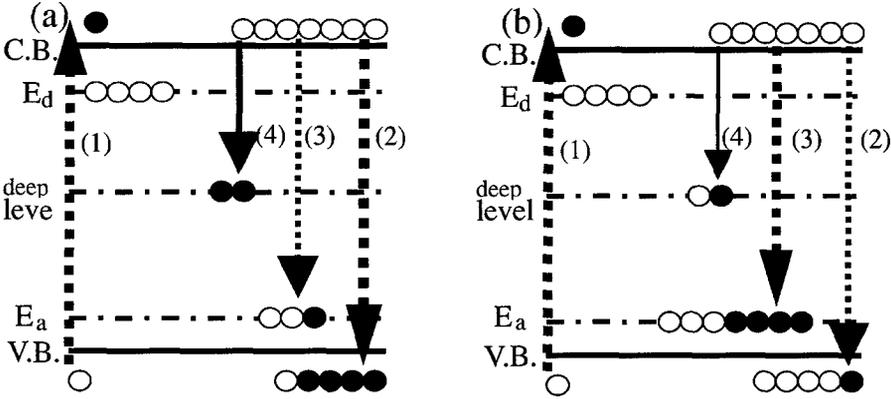
Figure 4. Schematic model of before Zn dope (a) and after Zn dope (b) in the active layer.

CONCLUSION

The PPTS measurements of InGaAlP LED with non- and Zn-doped active layers were carried out to investigate an effect of Zn-doping to the active layer. The results imply that the Zn atom doping creates not only a shallow acceptor but also deep defect levels at the same time in the InGaAlP active layer. The decrease of the PPT signal intensity with Zn doping for B band was explained by supposing that the shallow level was easily formed than the deep levels. However, the present model cannot reach the conclusion that the light emission efficiency of the present LEDs decreases with Zn doping. More detailed experiments should be carried out for further discussions.

ACKNOWLEDGMENT

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