Optical Mode Modulation of AlGaInP Multi Quantum Well Laser Diodes

Chih-Tsang Hung, Shen-Che Huang, Tien-Chang Lu
Department of Photonics & Institute of Electro-Optical Engineering, National Chiao Tung
University, Hsinchu 30050, Taiwan

ABSTRACT

We investigate the influence of passivation structure on the optical mode distribution and LI characteristics for the edge emitting AlGaInP-GaInP visible laser diode (LD). For traditional single-layer Si_3N_4 or SiO_2 passivation designs, the modification of dielectric layer thickness can determinate the lateral near-field confinement and change the horizontal far-field (FF) divergence. By increasing the film thickness, the non-radiation absorption come from Au-Ti can be improved and it leads to a narrow FF divergence beam. As continue to increasing the thickness, thicker passivation provides a better confinement factor and then the far-field pattern turn to be wider. For LI characteristics, it is necessary to deposit a thick enough passivation to reduce metal absorption. However, it cause much thermal energy accumulated in the ridge waveguide and deteriorate the quantum efficiency as adopting a too thick dielectric layer. Finally, we demonstrate a high power AlGaInP-GaInP multi quantum wells (MQWs) LD adopted a high-reflectivity passivation to enhance the LI characteristics and keep a suitable far-field divergence angle simultaneously. Under the design of three-pair optical thin films, it cannot only avoid the metal absorption but also enhance emitting efficiency and heat dissipation by using a high reflective and good thermal conductive Al_2O_3/Ta_2O_5 multilayer. The measured room-temperature threshold current (I_{th}) and characteristic temperature (I_{th}) can be arrived 44.5mA and 104.2K at 16.4° far-field divergence.

Keywords- AlGaInP, laser diodes, quantum-well lasers, dielectric layer, mode modulation

1. INTRODUCTION

High efficiency AlGaInP-GaInP visible laser diodes (LDs) are critical components for applications such as laser display, distance measurement instrument, and photodynamic therapy for the therapy of cancer. In order to achieve high performance single mode operation, typical AlGaInP LD structure utilized GaAs regrowth or narrow ridge strip design for lateral carrier and optical confinement [1]. However, these designs often lead to a low quantum efficiency or too high facet power density due to optical absorption loss in the GaAs second-growth layers. Hence, it is hard to achieve high-power operation in the AlGaInP-based laser diodes. This can be addressed by use of wider bandgap regrown materials, such as AlInP or AlGaInP, to construct an index guided laser structure [2]. Nevertheless, this design results in more complex crystal regrowth procedures and there are more defects occurring around the interface between these heterostructures. It leads to raising the proportion of non-radiation absorption and scattering loss, which also deteriorating the quantum efficiency. On the other hand, buried AlAs native oxides are adopted for carrier and optical confinement [3], [4], [5]. Although the design can improve scattering loss and absorption around the edge of ridge waveguide, the high temperature treatment leads to the variation of doping profile in the epitaxial layers during lateral wet oxidation and it affects the operation stability of laser characteristics directly.

In the investigation, we demonstrated a high-power AlGaInP-GaInP multi quantum wells (MQWs) LD adopted multilayer thin films as passivation layers to modify the lateral optical mode distribution, which can be operated with a low threshold current density and high conversion efficiency under a single mode operation. For a traditional ridge waveguide structure of the AlGaInP-GaInP red laser diodes, the single-layer dielectric thin film is often chose as passivation layers, such as SiO₂ or Si₃N₄ [6], [7]. For the single-layer passivation processing, most researches focuse on the adhesion around the interface and suppression of current leakage. There are few articles discussing about their influence on the power-

Nanoengineering: Fabrication, Properties, Optics, and Devices X, edited by Eva M. Campo, Elizabeth A. Dobisz, Louay A. Eldada, Proc. of SPIE Vol. 8816, 88160L · © 2013 SPIE CCC code: 0277-786X/13/\$18 · doi: 10.1117/12.2024042

Proc. of SPIE Vol. 8816 88160L-1

current (L-I) characteristics and optical confinement in the lateral transverse mode. We think the structural modification of dielectric thin film can play an important role to adjust the near-field (NF) optical mode distribution of edge emitting LDs since it is the major buffer region between the semiconductor and air. To observe the effect of passivation layer modification on the characteristics of lateral optical field, we adopt SiO₂ and Si₃N₄ fabricated from Plasma-enhanced chemical vapor deposition (PECVD) separately and set several thicknesses to deposit the dielectric thin film on the wafer surface after completing lateral waveguide etching process. By modifying the thickness of passivation layers, we can obtain the optimal lateral optical confinement but it is difficult to achieve a better L-I characteristics simultaneously at a stable working situation. In order to elevate the laser characteristics further, we design a high reflectivity dielectric layer which consists of multi-layer optical thin film to replace conventional structure of single-layer passivation. Using on the design of high-reflectivity passivation for the ridge waveguide LDs, it causes a suitable lateral optical confinement in near-field distribution and laser conversion efficiency can be effectively improved under a high-power operation.

2. EXPERIMENT DESIGN AND SIMULATION

Schematics of AlGaInP-GaInP edge emitting laser diode for 650-nm band are shown in Fig. 1. We adopt a GaAs substrate with high n-type doping and the layer sequence consists of an n-type 1.3 µm-thick n-type Al_{0.7}Ga_{0.3}InP bottom cladding layer, an AlGaInP-GaInP active region followed by a 1.3 µm-thick p-type top cladding layer with a asymmetric Al_{0.68}Ga_{0.32}InP composition. Above the p-cladding layer, high level carbon doped GaAs cap layer was used for the subsequent ohmic contact. The active region containing two-pair strain-compensated GaInP-Al_{0.5}Ga_{0.5}InP multi-quantum wells (MQWs) with a targeted thickness and composition to achieve the lasing wavelength of 650 nm is embedded in the separate confinement heterostucture (SCH) made from two 75-nm-thick Al_{0.5}Ga_{0.5}InP layers. The stripe profile of ridge waveguide was set to be trapezoid-shape with $3.2 \mu \text{ m/s} \mu \text{ m}$ for the top/bottom widths. For the passivation layers, we separately adopt single-layer and multi-layers structural designs which parameters are listed in Table. 1. The multi-layer passivation is designed by the principle of distributed Bragg reflector (DBR), which is consisted of three-pair optical thin films with high/low refractive index (Al₂O₃ 101.6nm/Ta₂O₅ 77.4nm, SiO₂ 112.1nm/TiO₂ 73.8nm). P/N-side metallization is set as Ti-Au and Ge-Au, respectively. The cavity length was chosen as 1000 um. Modeling of the near-field optical mode profiles and laser diode characteristics was performed by using the two-dimensional optical mode solver coded by the transfer matrix method and the standard laser rate equations adopting reasonable material gain coefficient in the GaInP MQWs. The far-field light pattern was calculated by simple Fourier transform of the near-field optical profiles. We analysis the far-field optical profiles in the horizontal direction by comparing the full width at half maximum (FWHM) of divergence angles, which is presented in Fig. 2.

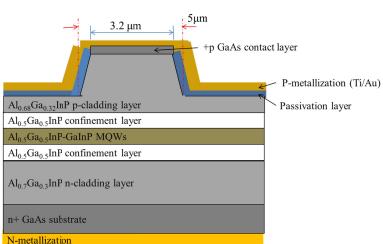


Fig. 1. The full structure of an AlGaInP-GaInP MQWs laser diodes which contains a GaAs substrate, an n-type $Al_{0.7}Ga_{0.3}InP$ bottom cladding layer, AlGaInP-GaInP MQWs surrounded by two $Al_{0.5}Ga_{0.5}InP$ optical confinement layers followed by a p-type $Al_{0.68}Ga_{0.32}InP$ top cladding layer, and a p-type GaAs cap layer

	No.	Material	Thickness [nm]	Reflectivity [%]	Thin film characteristics
)	1	PECVD Si ₃ N ₄	50	12.4	n=2.05 κ=16 [W/m-K]
	2		81	0.9	
	3		120	16.7	
	4		162	29.8	
	5		243	19.4	
	6		324	25	
	7		400	1.3	
	8	PECVD SiO ₂	50	21.4	n=1.46 κ=1.1 [W/m-K]
	9		81	11	
	10		113	5.6	
	11		170	20.1	
	12		226	29.7	
	13		282	18.8	
	14		400	21.9	
	15	Optical coating Al ₂ O ₃ /Ta ₂ O ₅	537	80.1	n=1.61/2.10 κ=3.3/33 [W/m-K]
	16	Optical coating SiO ₂ /TiO ₂	558	90.1	n=1.45/2.20 κ=1.0/1.15 [W/m-K]

Table 1. the structural parameters of passivation layers [8], [9].

First, we choose Si₃N₄ and SiO₂ as a single-layer passivation and modify film thickness to observe the influence on the modeling characteristics of optical field in the horizontal FF divergence patterns. Fig. 3(a) shows the calculated far-field FWHM of AlGaInP-GaInP LDs as a function of the thickness of dielectric layers. Comparing with the distribution of optical field in the LDs coated by the dielectric films with different thickness, the FF patterns exhibit a broad horizontal divergence angle as the thickness of dielectric film is less than 100nm. For the LDs which waveguide surrounded by Si₃N₄ and SiO₂, their far-field divergence angle is separately 14.0° and 17.0° under a 50-nm-thick passivation. There is some portion of emitting light absorbed by the titanium of p-metallization if the dielectric film is deposited with a too thin thickness. Due to the non-radiation absorption around the edge of ridge waveguide, the near-field optical mode becomes narrow in the lateral direction and it results to a wider horizontal divergence angle in the far-field pattern. By increasing the thickness of dielectric thin films, the metal absorption effect can be reduced gradually and hence the distribution of near-field lateral mode becomes broad simultaneously. The corresponding FF horizontal divergence angle can change into a wide FWHM through Fourier transform of the near-field optical profiles. Therefore, there is an obvious valley point happening in the diagram of FWHM curve as the thickness of dielectric film is increased from 50nm to 120nm. The minimum FWHMs of LDs covered with two dielectric films are 14.8° and 16.8°, respectively. When we keep raising the thickness of passivation, it is effective to enhance the lateral optical confinement and contributes to broaden the FF mode profile. Hence, the value of FWHM rises gradually as we increase the thickness from 120nm to 400nm. The widest divergence beam can be obtained at 400-nm-thick dielectric films, which is separately 16.3° and 17.9° for Si₃N₄ and SiO₂. Comparing with two series of samples coated by different dielectric layers, LDs covered with SiO₂ passivation possess a stronger lateral confinement and then the far-field FWHM become small since SiO₂ is provided with a lower refractive index (n=1.45) than that of Si₃N₄ (n=2.05). By analysising the results of two single-layer passivation, we find the trend of FWHM rising become slow when we increase the thickness close to 400nm. We think that the influence of thickness variation on the lateral optical confinement will trend toward a weak situation if the passivation layer is thicker than a critical value.

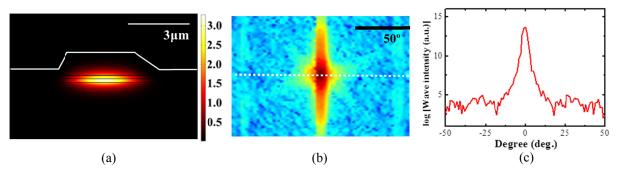


Fig. 2. (a) Calculated near-field optical mode distribution for the AlGaInP-GaInP LDs. (b) far-field light pattern transformed from the near-field optical profile. (c) intensity distribution of optical field in the horizontal far-field direction.

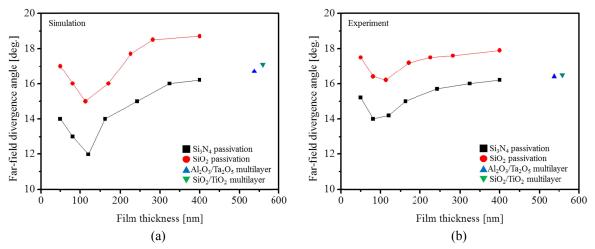


Fig. 3. (a) Simulated and (b) experimental far-field divergence angle measured at room temperature as a function of the thickness of passivation layers constituted by Si₃N₄, SiO₂ and multi-layer optical films.

For the multi-layer passivation, we separately adopt three-pair Al_2O_3/Ta_2O_5 and SiO_2/TiO_2 DBR films to replace the single-layer dielectric film. The total thicknesses of two multilayers are 537nm and 558nm, which is thicker than all of the single-layer samples. Since we adopt two materials possessing high/low refractive index, the effective index can be controlled within a lower value. Under this design, it is benefit to decrease the power density around the emitting mirror due to a low lateral confinement. The far-field FWHM of LDs coated with multilayers can still keep within 17° although the film thickness rise beyond 400nm.

3. RESULTS AND DISCUSSION

According to the structure design of device modeling, we fabricated the AlGaInP-GaInP MQWs LDs in a low pressure metal-organic chemical vapor (MOCVD) system. All the epitaxial layers were grown on (100) n-type GaAs substrates with Si as the n-type dopant, Zn as the p-type dopant in the cladding layers and C as the p-type dopant in the contact layer. Narrow stripe (top/bottom width= $3.2/5~\mu$ m) ridge waveguide laser structures were manufactured by chemical wet etching. On the basis of the above-mentioned conditions of passivation , we deposit the single-layer dielectric film of Si₃N₄, SiO₂, and multi-layer passivation by PECVD and electron beam (e-beam) evaporation after lateral ridge waveguide etching processing. The corresponding structural parameters are listed in Table. 1. In order to prevent the facet from catastrophic optical damage (COD) during high power operation, window mirror region was made by using disordering of quantum well with zinc diffusion. For selective current injection into a laser stripe, a GaAs contact layer was etched off and the passivation film was deposited at outside of a narrow stripe active area. Ti/Au and AuGe/Au metallization were applied as p-side and n-side contacts, respectively. By Laser chips were cleaved and covered with antioxidant passivation so that the cavity length was $1000~\mu$ m. The facets were AR/HR coated by e-beam evaporation with Al₂O₃/TiO₂ multilayers. The devices were cut into laser bars and tested on Cu heat sinks. A detailed schematic drawing of fabricated LD is shown in Fig. 5(a). Fig. 5(b) and 5(c) exhibit the cross sections of SEM images at the laser facet for LDs covered with the Si₃N₄ and three-pair Al₂O₃/Ta₂O₅ passivation, respectively.

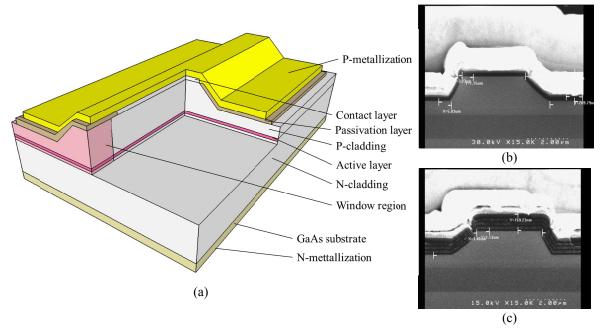


Fig. 4 (a) Schematic of the fabricated LD. The SEM cross section images of LDs covered with (b) Si_3N_4 dielectric layer and (c) Al_2O_3/Ta_2O_5 multilayers.

CW characteristics of both types LDs were measured at operation temperatures of 25, 40, 50, 60, 70°C and horizontal far-field patterns were taken by the corrected charge-coupled device (CCD) camera under 120-mW working power. In Fig. 3(b), only fundamental transverse modes with no trace of higher order modes have been observed in the LDs, which are similar to the modeling results of the optical field distribution. For single-layer Si₃N₄ passivation, there will be nonradiation absorption occurring around the edge of ridge waveguide if we deposit a too thin Si₃N₄ thin film between the interface of p-metallization and semiconductor. The absorption effect come from the Ti-Au alloy leads to a narrow lateral near-field optical mode and then contributes to a wide far-field divergence pattern. Comparing to the modeling results, the influence of metal absorption is more serious in the actual experiments and hence the measured divergence angle exhibit a larger value (FWHM = 15.2°) under 50-nm-thick Si₃N₄ passivation. As increasing thickness from 50nm to 100nm, the absorption effect become weak gradually and the lateral optical profile exhibit a broader distribution. Due to broadening of lateral optical mode, we can obtain a valley point of FWHM curve located at 100nm Si₃N₄ passivation (FWHM $\sim 13.9^{\circ}$). When we continue to increase the thickness of Si₂N₄ dielectric film to 400nm, the horizontal FF divergence angle rise from 13.9° to 16.2° . The main reason is that the thicker passivation layer provides a better lateral optical confinement of near-field optical mode, and it contributes to a broadening effect on the horizontal far-field pattern by Fourier transform. Similar to the calculated results, the rate of divergence angle variation become slow and the value of FWHM seem to be arrive a saturation status as the thickness is increased close to 400nm. The same trend of FWHM variation can be obtained from the LDs coated by SiO₂ dielectric layer. By reducing the metal absorption, we can obtain a minimum value of FF divergence angle (FWHM= 16.2°) at 113-nm-thick SiO₂ passivation. Comparing with Si₃N₄, the lower refractive index of SiO₂ thin film fabricated by PECVE causes a stronger lateral optical confinement and the wider far-field FWHM can be obtained under the same thickness of passivation layers. As adopting the multi-layer passivation consisted of high-reflectivity DBR, the film thickness is thick enough to avoid the non-radiation absorption come from the Ti-Au metallization. Since using the combination of high/low refractive-index materials, the lateral confinement factor can be controlled within a suitable range and hence the mode profile does not show a too concentrated distribution. It is workable to reduce the power density around the laser emitting facet, which causing a higher COD level. The far-field divergence angles of LDs are separately 16.4° and 16.5° for ridge waveguides surrounded by Al₂O₃/Ta₂O₅ and SiO₂/TiO₂ DBRs.

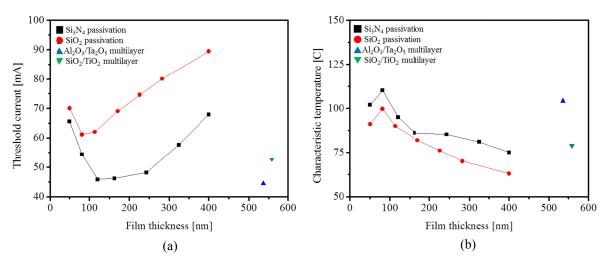


Fig. 5. The threshold current and characteristic temperature as a function of the thickness of passivation layers constituted by Si_3N_4 , SiO_2 and multi-layer optical films.

For the L-I measurement results shown in Fig. 5, they include the variation of threshold current (I_{th}) and characteristic temperature with the passivation thickness at room-temperature operation. While the thickness of Si_3N_4 film is set less than 120nm, the corresponding threshold current exhibit an increasing trend with the raising of film thickness. Under a thin passivation, Ti-Au alloy probably absorbs some emitting light of near-field optical mode around the edge of ridge waveguide. Since the non-radiation absorption causes a drop of external quantum efficiency, the corresponding I_{th} show a high value during high-power operation. When the thickness is increased beyond 120nm, we can effectively reduce

threshold current less than 50mA due to the reduction of metal absorption. Therefore, the threshold current can be kept within 50mA as the passivation thickness distributes in the range of 120-200nm. While we continue to increase the film thickness from 150nm to 400nm, the room-temperature threshold current of LDs rise rapidly close to 70mA. There might be more residual heat accumulating within the ridge waveguide during high-power operation as depositing a thicker passivation film on the interface between the semiconductor and p-metallization. Under this situation, the accumulated thermal energy leads to electron overflow from the MQWs region and then carrier injection efficiency become low obvious, especially under high-temperature or high-power CW operation. Analyzing the SiO₂ samples, it presents a similar result under a thin passivation. The alteration of threshold current is dominated by the metal absorption. However, the threshold current of the LDs coated with SiO₂ is higher than that of Si₃N₄ under the same film thickness due to the worse thermal conductivity of SiO₂. For Si₃N₄ and SiO₂ fabricated by PECVD, the measured values of thermal conductivity are separately 1.1 and 16 W/m-K. Hence, the carrier thermal overflow must get serious as we adopt a thick SiO₂ dielectric layer. The value of threshold current increases from 61.2mA to 89.5mA with raising the thickness of passivation layer from 100nm to 400nm. Compare with two series of LI curves in Fig. 6, the Si₃N₄ samples do not only possess a lower threshold current but also exhibit a better slope efficiency under various film thicknesses. As adopting a thick dielectric passivation, we can find that there are some power-kinks appearing as the lasing power rise to 120mW. The maximum output power of LDs covered with 400-nm-thick SiO₂ even cannot arrives 120mW, and we can observe many kink happen in its LI curve.

The temperature characteristics are defined using the T_0 that are the measures of temperature sensitivity to threshold current at 120mW working power, expressed as $I_{th} = I_{th}(0) \exp(\Delta T/T_0)$, where $I_{th}(0)$ and I_{th} are threshold currents before and after changing the operation temperature, and ΔT is the variation of temperature. As raising working temperature form 25°C to 70°C , both of characteristic temperatures come from the LDs covered by two single-layer passivation show the same varying trend. As shown in Fig. 5(b), we find the T_0 drop more obviously under a thicker dielectric film. It indicate that the influence of residual heat on the L-I characteristics is more serious than that of metal absorption. Hence, the LDs coated with Si_3N_4 possess better characteristic temperatures because of the higher thermal conductivity. Basing on an optimal passivation design of single-layer dielectric film, we can obtain a maximum value of 110.2k and 99.8k under 81-nm-thick Si_3N_4 and SiO_2 .

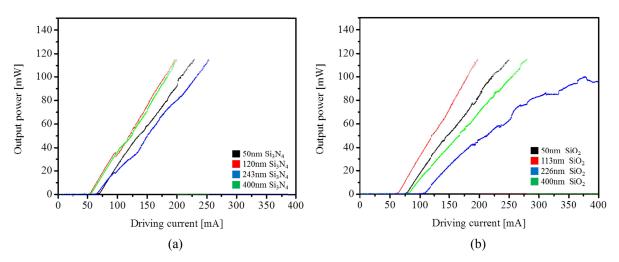


Fig. 6. The influence of passivation thickness on the L-I characteristics of ridge waveguide LDs covered with (a) Si_3N_4 and (b) SiO_2 dielectric layers.

On the other hand, the LDs adopted three-pair optical thin films as passivation still possess relatively low threshold current although the heat accumulation should affect the LI characteristics since the total thicknesses of passivation films are thicker than 400nm. As shown in Fig. 5(a), the room-temperature threshold currents are separately 44.5mA and 52.6mA for the LDs deposited with Al₂O₃/Ta₂O₅ and SiO₂/TiO₂ multilayers. These values might be better than those of LDs coated with Si₃N₄ and SiO₂ single-layers under the same film thickness. Basing on a high-reflectivity interface between the semiconductor and p-metallization, there are more emitting light confined within waveguide since the DBR

interface can avoid optical beam scattering out of the ridge stripe. It is workable to enhance the quantum efficiency and contribute to improvement of threshold current. By referring to the detailed data of thermal conductivity listed in the Table. 1, the I_{th} of Al_2O_3/Ta_2O_5 passivation is lower than that of SiO_2/TiO_2 multilayer due to the better thermal conductivity. To observe the difference of characteristic temperature, we find the T_0 of Al_2O_3/Ta_2O_5 samples is also much better than that of SiO_2/TiO_2 multilayers (104.02K > 79.06K). It also proves that the influence of passivation thermal conductivity on laser L-I characteristics is very important at high-power operation. Comparing the two L-I curve operated at a 120-mW working power, both of threshold current and slope efficiency are better as adopting Al_2O_3/Ta_2O_5 passivation, as shown in Fig. 7. In addition, there are not power-kinks appearing in the LI curve since the good heat-dissipation structure contributes to a stable distribution of optical mode.

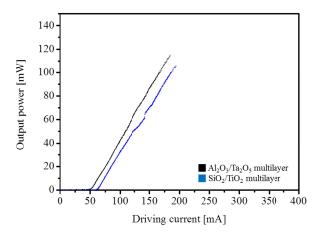


Fig. 7. The L-I characteristics of LDs coated with Al₂O₃/Ta₂O₅ and SiO₂/TiO₂ multi-layer passivation.

4. CONCLUSIONS

High-power AlGaInP-GaInP multi quantum wells (MQWs) LD adopted an Al_2O_3/Ta_2O_5 DBR as a passivation to obtain stable lateral optical mode distribution and optimize the L-I characteristics demonstrated low threshold current and high conversion efficiency under a single mode operation. Compared to the conventional design of single-layer passivation, the three-pair multilayer provides a sufficient thickness to avoid the metal absorption and two kinds of optical thin films with high/low index weaken the lateral confinement to reduce power density at the laser facet. The design of high-reflectivity interface can improve the scattering loss and it is benefit to decrease the threshold current and raise the conversion efficiency. Since Al_2O_3/Ta_2O_5 multilayer possesses a better thermal conductivity, it contributes to a better temperature characteristic and makes the LDs more suitable to work under high-power and high-temperature operation. The measured room-temperature threshold current and characteristic temperature can be arrived 44.5mA and 104.2K without any power-kink at 16.4° far-field divergence.

ACKNOWLEDGMENT

This work was supported in part by the Ministry of Education Aim for the Top University program and by the National Science Council of Taiwan under Contract No. NSC99-2622-E009-009-CC3 and NSC98-2923-E-009-001-MY3.

REFERENCES

- [1] M. Ishikawa, Y. Ohba, Y. Watanabe, H. Nagasaki, H. Sugawara, M. Yamamoto, and G. Hatakoshi, "InGaAlP transverse mode stabilized visible laser diodes fabricated by MOCVD selective growth," in Est. Abstracts 18th Int. Conf. Solid State Devices and Materials, Toyko, Japan, 1986, pp. 153–156.
- [2] R. Kobayashi, H. Hotta, F. Miyasaka, K. Hara, and K. Kobayashi, "Real index-guided AlGaInP visible laser with high-bandgap energy AlInP current blocking layer grown by HCl-assisted metalorganic vapor phase epitaxy," IEEE J. Select. Topics Quantum Electron., vol. 1, pp. 723–727, 1995.

Proc. of SPIE Vol. 8816 88160L-7

- [3] S. A. Maranowski, A. R. Sugg, E. I. Chen, and N. Holonyak, Jr., "Native oxide top-and bottom confined narrow stripe p-n Al y Ga 1 0 y As-GaAs-In x Ga 1 0 x As quantum well heterostructure laser," Appl. Phys. Lett., vol. 63, 1993, pp. 1660–1162.
- [4] Y. Cheng, P. D. Dapkus, M. H. MacDougal, and G. M. Yang, "Lasing characteristics of high-performance narrow-stripe InGaAs-GaAs quantum-well lasers confined by AlAs native oxide," IEEE Photon. Technol. Lett., vol. 8, pp. 176–178, 1996.
- [5] P. D. Floyd, D. Sun, and D. W. Treat "Low-Threshold Laterally Oxidized GaInP-AlGaInP Quantum-Well Laser Diodes" IEEE Photonics Technology Letters, vol. 10, no. 1, 1998
- [6] D. P. Bour , K. J. Beernink and D. W. Treat "AlGaInP single quantum well laser diodes," SPIE Visible and UV Lasers, vol. 2115, pp.269-280 1994
- [7] S. A. Wood, P. M. Smowton, C. H. Molloy, P. Blood and D. J. Somerford "Direct monitoring of thermally activated leakage current in AlGaInP laser diodes," Appl. Phys. Lett., vol. 74, pp.2540-2542 1999
- [8] Gorodetsky, M.L., "Thermal noises and noise compensation in high reflection multilayer coating," Phys. Lett. A, 2008. 372: p. 6813-6822.
- [9] Mun J., Kim S. W., Kato R., Hatta I., et al., "Measurement of the thermal conductivity of TiO2 thin films by using the thermo-reflectance method" Thermochimica acta, 2007. 455(1-2): p. 55-59.