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Al$_x$Ga$_{1-x}$As/Al$_y$Ga$_{1-y}$As VISIBLE LASERS GROWN BY MOCVD

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Abstract. -- AlGaAs/AlGaAs double-heterostructure (DH) visible lasers with low threshold current densities have been grown by metalorganic chemical vapor deposition (MOCVD). Proton-isolated narrow stripe visible lasers have good performance and uniformity of the characteristics over the whole wafer is excellent. Contamination of the undoped AlGaAs depends on the partial pressure ratio of V element to III elements as well as on Al content. Carbon and oxygen contamination is most essential and discussed in detail. Finally, some systematic results of life test for the MOCVD visible lasers will be presented.

1. Introduction. -- AlGaAs/GaAs double-heterostructure (DH) laser with a low threshold current density was made by Dupuis and Dapkus using metalorganic chemical vapor deposition (MOCVD). They also fabricated single- and multi-quantum well heterostructure lasers with unique laser characteristics by the MOCVD technology. Their successes demonstrated capability of MOCVD for growing high quality AlGaAs and its excellent controllability comparable to molecular beam epitaxy technology. MOCVD-grown AlGaAs/GaAs DH visible lasers with emission wavelength down to 760 nm were obtained by Mori and Watanabe. Both the threshold currents and degradation rates were, however, larger than that of the lasers with GaAs active layer. This result indicated that the growth of high quality AlGaAs is much more difficult than that for GaAs. Stringfellow, et al. have intensively investigated optical and electrical properties of MOCVD-grown AlGaAs, especially, carbon and oxygen incorporation into the AlGaAs. They found a method for gettering of residual oxygen, and also investigated optimum growth conditions to obtain high quality AlGaAs in MOCVD. Recently, MOCVD-grown visible lasers with emission wavelength down to 715 nm have been fabricated. More recently, Burnham, et al. have reported very short wavelength lasers down to 700 nm with very low threshold current densities. These results clearly indicate that the MOCVD process is a very useful technology to prepare excellent quality AlGaAs and that there are no essential problems to obtain low cost DH visible lasers for practical use.

This paper will describe some experimental results suggesting an optimum V/III ratio in the growth ambient to reduce carbon contamination in AlGaAs, and an influence of residual impurity in an AsH$_3$/H$_2$ on the quality of AlGaAs. Structure, device performance of narrow stripe visible lasers and uniformity of their properties over a whole wafer are also reported. Finally, results of some systematic life tests for our visible lasers will be presented, which is the first systematic result of accelerated life tests for MOCVD-grown lasers.

2. Epitaxial Growth and Quality of the Layer.

2.1 Optimum V/III Mole Ratio. -- An arsenic over pressure, i.e., V/III mole ratio, and growth temperature are the most important parameters to obtain high purity GaAs and AlGaAs by MOCVD. As previously observed, the conduction type of the undoped GaAs changes from p to n as the V/III ratio and/or growth temperature increased. Several impurities, i.e., Si, C, Zn and others, have been considered to cause the type change. We have studied in detail the dependence of each impurity
concentration incorporated in the undoped materials on the V/III ratio, and we found that the total impurity concentration was minimized when the materials were grown under the V/III ratio near the p/n transition.

Carrier concentration in undoped Al$_x$Ga$_{1-x}$As grown at 800°C against the mole fraction, x, is shown in Fig. 1. The hole concentration increased steeply with x at a fixed V/III ratio in the p-type region, and the electron concentration increased proportionally with x in the n-type region. Hence the V/III ratio at the p/n transition shifts to higher region with increasing x as shown in Fig. 2.

Typical photoluminescence (PL) spectra for undoped n-type GaAs and Al$_{0.1}$Ga$_{0.9}$As at 77 K are shown in Fig. 3. Three peaks ($A_1; 25$ meV, $A_2; 35$ meV, and $A_3; 152$ meV) due to acceptors are always present in all the GaAs samples. With Al addition, an additional acceptor peak denoted $A_4$ ($; 90$ meV) was introduced. Relative intensity of the $A_4$ to the band-edge emission peak (B) was found to increase exponentially with AlAs mole fraction. While the peak intensity of $A_3$ scattered considerably from lot to lot of the AsH$_3$/H$_2$ gas cylinder, other acceptor peak intensities were much less scattered, and changed monotonically by changing the V/III ratio.

![FIG. 1: Relation of the carrier concentration in undoped Al$_x$Ga$_{1-x}$As to the AlAs mole fraction, x. Solid and dashed lines are for the samples grown under the V/III ratio 40 and 4, respectively.](image1)

![FIG. 2: Carrier concentration in undoped samples to the V/III ratio for various X.](image2)

![FIG. 3: Typical photoluminescence (PL) spectra for n-type GaAs and Al$_{0.1}$Ga$_{0.9}$As at 77K.](image3)
The impurity $A_3$ is Cu which might be introduced mainly from the AsH$_3$/H$_2$ gas cylinder. Impurity $A_4$ would be Mn which is introduced from trimethylaluminum (TMA). Impurity $A_1$ may be C, which is dominant impurity in MOCVD grown layer. $A_2$ impurity would be Zn which comes from trimethylgallium (TMG) and TMA.

The peak intensity of the main acceptor carbon relative to the B peak, which gives the relative concentration, $N_{Al} = kN_D (I_{Al}/I_B)$, is plotted against the V/III ratio in Fig. 4. If we assume $k$ value is not much different with Al addition, concentration of C is higher in AlGaAs than in GaAs, and it increases exponentially with $x$, which is reflected as increase of hole concentration in Fig. 1.

Concentration of each impurity was separately determined for a range of V/III ratio by combining data on the relative PL intensities with the carrier concentration measured electrically. From the result, the total impurity concentration was found to be minimized near the V/III ratio of the p/n transition. Similar calculation was applied for AlGaAs, and we obtained the optimum V/III ratio depending on the AlAs mole fraction as shown in Fig. 5.

![Fig. 4: Intensity ratios of the PL peak due to acceptor (Al) to that of the band-edge emission (B).](image)

![Fig. 5: Optimum V/III ratio to reduce total shallow impurity concentrations in Al$_x$Ga$_{1-x}$As against $x$.](image)

2.2. Oxygen contamination in AlGaAs. As far as we consider the shallow impurities, the optimum V/III ratio for AlGaAs is so high, that it reaches as high as 100 for Al$_{0.5}$Ga$_{0.7}$As. However, it is necessary to include deep trap impurities to obtain truly optimized condition. As previously observed, the impurity oxygen incorporated into the AlGaAs acts as a deep trap and decreases PL intensity of the crystal. Impurity oxygen and/or water vapor, in our case, comes mainly from AsH$_3$/H$_2$ gas cylinder, and the ratio of partial pressure of oxygen and/or water vapor to the column III elements in the growth ambient increases with the V/III ratio. Then the optimum V/III ratio should be different from the values in Fig. 5. Such optimum V/III ratio, unfortunately, can not be defined explicitly, because the concentration of oxygen and/or water vapor in AsH$_3$/H$_2$ changes from lot to lot of the cylinder. One of the experimental results related to the impurity in AsH$_3$/H$_2$ influencing the growth of AlGaAs is described below.
Dependence of the growth rate of AlAs on the V/III ratio for several different lots of AsH$_3$/H$_2$ is shown in Fig. 6. The growth rate of AlAs decreased significantly for some lot of AsH$_3$/H$_2$ as the V/III ratio was increased, while the growth rate of GaAs did not. The data show the significant difference in amount of impurity between the different lots of AsH$_3$/H$_2$. Figure 7 shows PL intensity of AlGaAs against the V/III ratio grown from relatively impure AsH$_3$/H$_2$ lot. The PL intensity normalized by the free carrier concentration decreased monotonically with the V/III ratio. Therefore, a lower V/III ratio is favorable to reduce oxygen and/or water vapor contamination in AlGaAs, which conflicts with the growth condition to reduce carbon contamination. While it is important to reduce contamination in an AsH$_3$/H$_2$ gas cylinder, it is necessary to make compromise between carbon and oxygen contaminations for an actual contaminated gas cylinder.

From these results, we concluded that the favorable V/III ratio must be defined from the incorporation ratio of carbon and oxygen, and it depends on purity and history of an AsH$_3$/H$_2$ gas cylinder.

The quality of AlGaAs grown under the favorable growth conditions defined from the above study is as good as the LPE crystals as shown in Fig. 8.
2.3. Uniformity - MOCVD is an excellent technology for uniform growth on a large-scaled wafer as reported by many authors. We have confirmed that uniform growth can be achieved by both a vertical and a horizontal reactors. Thickness variation of about 2.5 \( \mu \text{m} \) thick AlGaAs grown layer on a large-scaled wafer (-40 mm in large diameter) is less than \( \pm 1.5\% \), except the periphery, where edge growth occurred. An example is shown in Fig. 9, where the data was for the vertical reactor. In addition to layer thickness uniformity, doping density, alloy composition, electron mobility and PL intensity of Se doped Al\(_{0.3}\)Ga\(_{0.7}\)As layer are also excellent, as shown in the same figure. Variations of carrier concentration, mobility and PL intensity were less than 8.8, 3.0 and 3.7\%, respectively. A variation of the band-edge PL peak wavelength was less than 1 nm, which is a resolution limit of our spectrometer. Among them the variation of carrier concentration is the worst, which is probably due to nonuniformity of temperature over the susceptor.

We have studied on proton-isolated narrow stripe visible lasers for application to optical read-out purposes. Structure and performance of the lasers shall be described in more detail in the following section. Distribution of device characteristics shown in Fig. 10 illustrates the uniformity achieved by MOCVD. Figure 10 is a typical example of the variations of a threshold current and lasing wavelength for one bar with 35 devices of the visible lasers. These uniformities are good enough in practice. For instance, the standard deviation of the threshold current is less than 1.4\%.

3. Performance of Visible Lasers - Room temperature continuous-wave (cw) operation can be achieved by fabricating stripe geometry structures. MOCVD grown stripe geometry lasers with several different structures have been reported. A proton bombarded stripe geometry is a simplest way for current confinement and suitable for reproducible fabrication.
Figure 11 is a schematic view of the cross section of the proton-isolated DH laser structure. Typical thickness of the active and cladding layers are 0.15 and 1.0 \( \mu \text{m} \). The AlAs mole fraction in both layers varied from 0 to 0.31 and from 0.3 to 0.72, respectively. These layers were sequentially grown under the V/III ratio 25 - 30 at the growth temperature 750 - 8000°C. A 1 \( \mu \text{m} \) thick and 2 to 10 \( \mu \text{m} \) wide stripe gold layer on a p-side ohmic contact metal Au/Pt/Ti or Cr was used as a mask for proton bombardment. Typical accelerating energy of protons was 200 KeV. The high resistance region was typically formed to a depth of 0.5 \( \mu \text{m} \) above the active layer.

The relation of the pulsed threshold current to the emission wavelength for 200 \( \mu \text{m} \) long 10 \( \mu \text{m} \) wide stripe devices is shown in Fig. 12. The solid curve in the figure represents a theoretical variation of the threshold current calculated using band parameters given by Casey and Panish.\(^\text{15}\) The data were close to the theoretical curve. The shortest lasing wavelength achieved for pulsed operation was 683 nm. The minimum threshold current density measured for the broad contact device of 780 nm emission and 500 \( \mu \text{m} \) long cavity was 570 A/cm\(^2\). This is comparable to the best result obtained so far for the MOCVD grown laser with a GaAs active layer.\(^\text{16}\) Figure 13 shows typical relations of light-output power versus dc driving current (L - I) for devices with emission wavelength 787 nm and 725 nm. Current-voltage relationships for the devices were almost the same, which indicates good doping characteristics in the cladding layers with high AlAs mole fraction. Though the threshold current is almost independent both of the stripe width and of the depth of the proton bombarded region, the linearity of L - I characteristics improves as the strip width decreases. The dc output power increased linearly without kinks up to 10 mW/facet for 5 \( \mu \text{m} \) strip devices even when the emission wavelength was shorter than 725 nm. Differential quantum efficiency of the laser greater than 60% was found to be almost independent both of the stripe width and of the emission wavelength. This value is larger than that of lasers with the same geometry grown by LPE.

\[ \text{Au} \quad \text{P-GaAs} \quad \text{P-Al}_{x}\text{Ga}_{1-x}\text{As} \quad \text{P-Al}_{x}\text{Ga}_{1-x}\text{As} \quad \text{n-Al}_{x}\text{Ga}_{1-x}\text{As} \quad \text{n-GaAs} \quad \text{n-GaAs sub} \]

\[ \text{Proton bombarded} \]

FIG. 11 : Schematic cross section of the proton isolated visible laser.

\[ \text{W 8 - 10 \( \mu \text{m} \)} \quad \text{L 200 \( \mu \text{m} \)} \]

\[ \text{THRESHOLD CURRENT (mA)} \]

\[ \text{WAVELENGTH (nm)} \]

\[ \text{Calc.} \]

FIG. 12 : Threshold current of MOCVD grown proton isolated laser versus the emission wavelength.

\[ \text{OUTPUT POWER (mW/facet)} \]

\[ \text{W 8\mu m} \quad \text{L 250 \( \mu \text{m} \)} \]

\[ \text{787 nm} \quad \text{725 nm} \]

\[ \text{CURRENT (mA)} \]

FIG. 13 : Typical relations of the light-output power to the dc current.
4. Lifetimes of MOCVD Visible Lasers - It is of great practical importance to obtain long life DH lasers by MOCVD. A lifetime of more than 5000h at about 50°C is generally required for practical use. However, a systematic result of accelerated life tests for MOCVD lasers has not yet been reported. Results on preliminary life tests were reported for several types of cw lasers. For example, stripe-geometry quantum-well heterostructure lasers have achieved cw operation for over 3200h.\(^{17}\) Oxide-isolated planar stripe lasers operated for more than 9000h at an output power lower than 1 mW/facet.\(^{16}\) Single mode lasers with a V-shaped active layer operated with an output power of 4 mW/facet for more than 4000h.\(^{18}\)

We have carried out accelerated life tests for proton isolated narrow stripe visible lasers at the ambient temperatures of 30, 50 and 70°C in the air. The non-screened devices with a plasma deposited SiN coating were operated at the constant power of 3 mW/facet. Variation of diode driving current as a function of operating time at 50°C is shown in Fig. 14. Many of these devices are now operating for more than 5000h with a degradation rate of the order of \(10^{-5}\text{h}^{-1}\). Preliminary test devices have operated for more than 7000h at 50°C and now operating stably.

Furthermore, about half the number of devices are operating over 5000h at 70°C.

![Variation of the diode driving current as a function of the operation time for non-screened samples at 50°C.](image1)

**FIG. 14**: Variation of the diode driving current as a function of the operation time for non-screened samples at 50°C.

![Median lifetime to the inverse ambient temperature for 787 nm devices.](image2)

**FIG. 15**: Median lifetime to the inverse ambient temperature for 787 nm devices.

Figure 15 shows the relation of the median life time to the inverse ambient temperature for 787 nm devices. The activation energy of failure, \(E_a\), deduced from the slope is 0.61 eV. The activation energy reported for the LPE grown devices ranges from 0.5 to 1.0 eV.\(^{19-21}\) Our value 0.61 eV is relatively low and not far from the value for light emitting diode.\(^{21-23}\) The median life time against the lasing wavelength is shown in Fig. 16. Data obtained for LPE devices reported by Kajimura et al.\(^{24}\) are also shown by dots in the figure for comparison. The wavelength dependence of failure is quite similar to that of LPE devices, which suggests some strong degradation mechanisms should exist for MOCVD shorter wavelength devices in common with LPE.

The lifetime of our MOCVD lasers with wide range of emission wavelength is comparable to that of LPE lasers.
5. Conclusions

We have investigated the relationship between crystal quality and the growth condition, i.e., partial pressure ratio of V to III elements in the growth ambient, in MOCVD. The concentration of the main acceptor impurity carbon incorporated in AlGaAs increased with AlAs mole fraction, and that decreased monotonically as the V/III ratio increased. Contamination of the residual impurity oxygen came from the \( \text{A}_3\text{H}_3/\text{H}_2 \) gas cylinder, on the other hand, increased with the V/III ratio. We found that the favorable V/III ratio to obtain a high quality AlGaAs in MOCVD should be defined from the incorporation ratio of carbon and oxygen, and it depended on the purity and history of the \( \text{A}_3\text{H}_3/\text{H}_2 \) gas cylinder. The quality of AlGaAs grown under the favorable growth conditions defined in this way was as good as the LPE crystals. We demonstrated the excellent uniformities of grown layer thickness, electrical and optical properties over the whole wafer, and also device characteristics. Low threshold visible lasers emitted down to 683 nm was obtained in pulsed operation. Linear relationship between the light-output power and dc driving current was observed up to 10 m W/facet for the proton isolated narrow stripe visible lasers. We have carried out for the first time accelerated life tests for the MOCVD visible lasers. The non-screened 787 nm devices have been operating stably for more than 5000 h with the degradation rate of the order of \( 10^{-5}\text{h}^{-1} \) at 50°C and 70°C.

The activation energy of failure obtained for 787 nm device was 0.61 eV, which is relatively low. The wavelength dependence of failure was quite similar to that of LPE devices.

The reliability of our MOCVD lasers with wide range of emission wavelength was comparable to that of LPE lasers. We concluded that the MOCVD is now one of the most useful technology for production of large-scale visible laser wafers with excellent performance and reliability.

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