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Carrier Concentration and Composition Profiling for GaAs/AlGaAs Laser Diodes

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Abstract

A computer controlled automatic carrier concentration profiler is used to assess GaAs/AlGaAs single layers and multilayers for laser diodes.

For the reliable profiling of high/low-doped multilayers and transition regions between epitaxy /semi-insulating substrate, the definition of electrolyte/semiconductor contact area becomes important, since the capacitance arising from excess side area becomes relatively large. This undesirable area is considerably reduced by using a thick photoresist or a light-tight wax with a large sealing ring, so that the profiling extending for 3 orders becomes possible even for small etching area of about 1 mm^2.

A simple and convenient composition profiling technique for $Al_XGa_{1-X}As$ layers, utilizing the photovoltaic effect of the electrolyte/semiconductor system is also described. The result is consistent with PL measurements.

Simultaneous profiling of the carrier concentration and Al composition is successfully done against GaAs/AlGaAs multilayers.

1. Introduction

In connection with the development and fabrication of sophisticated semiconductor devices such as GaAs/AlGaAs double heterostructure (DH) lasers, a rapid and reliable assessment of grown layers is required in order to establish optimum growth conditions. Basic and most important parameters of laser structure are carrier concentrations and Al composition. Recently, for measuring these parameters, a computer controlled automatic carrier concentration depth profiling system is widely used. Principles of the profiler are based on the electrochemical etching of the semiconductor surface and the subsequent C-V measurement of the Schottky barrier formed at the semiconductor/electrolyte interface[1,2], which allows continuous profiling of carrier concentration against depth. However, reliable profiling is sometimes difficult owing to excess capacitance arising from undefined side area, when a plastic sealing ring with small diameter is used for the definition of etching area. The use of the large sealing ring is one of methods to reduce the undesirable capacitance, but the method needs a large area extended over a few tens

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mm^2.

In this report, a different method to define electrolyte/semiconductor contact area using a thick photoresist or a light-tight wax combined with the sealing ring is described. This method considerably reduced excess side area, and reliable profiling of high/low-doped multilayers and epitaxy / semi-insulating substrate transition regions becomes possible even for small defined area below 1 mm^2.

The validity of determining Al composition in $Al_xGa_{1-x}As$ layers by simple and convenient photovoltage spectroscopy measurement is also studied by comparing photoluminescence data. Finally, the example of simultaneous profiling of the carrier concentration and Al composition is given for a GaAs/AlGaAs multilayer.

2. Experimental Technique

"Polaron PN 4200 Profile Plotter" (Bio-Rad Lab.) was used to assess GaAs and AlGaAs layers grown by MOCVD method. Briefly, the carrier concentration is first determined by measuring the electrolyte/semiconductor Schottky barrier capacitance. In its differentiated form, the carrier concentration N (W_d) at the end of the depletion layer is given by the following well-known equation;

$$N(W_d) = \frac{1}{q\varepsilon_0\varepsilon_s} \cdot \frac{C^3}{(dC/dV)} \cdot \frac{1}{A^2} \tag{1}$$

where q is the electronic charge, $\varepsilon_0\varepsilon_s$ is the permittivity of the semiconductor, A is the contact area, C is the depletion layer capacitance and V is the applied bias voltage. Both the capacitance and the differential capacitance, dC/dV, are measured by phase sensitive detectors. Then the profiler enters an etching cycle, during which a predetermined amount of sample is anodically dissolved. The thickness removed, W_r, can be obtained from the Faraday's low of electrolysis; that is,

$$W_r = \frac{M}{z\,F\,D\,A} \int I \cdot dt \tag{2}$$

where M is the molecular weight, z is the number of transferred carriers per molecule dissolved, F is the Faraday constant, D is the density and $\int Idt$ is the time integral of the dissolution current. Thus, the measurement depth x from the original surface is given by;

$$x = W_d + W_r \tag{3}$$

Since the contribution of holes to the anodic dissolution is almost unity, n-type sample is normally illuminated for the etching in order to supply sufficient holes.

For successful profiling of the carrier concentration, choice of the electrolyte appropriate for both etching and capacitance measurements is one of the most important factors.

To find a suitable electrolyte, several kinds of electrolytes such as Tiron (1, 2 dihydroxybenzene-3, 5 disulfonic acid, sodium salt solution), ammonium tartrate solutions, KOH, NaOH, H_3PO_4 mixed with glycol etc. were examined. In the experiment, the electrolyte/semiconductor contact area was typically set to 1 mm^2 and the anodic dissolution of n-type

samples was carried out by the photocurrent within the saturation region to induce a non-defect revealing etch[3]. Before and during the profiling of carrier concentration, I-V, C-V and G-V date, as shown in Fig. 1, were taken to judge the quality of the Schottky barrier formed, and to determine the correct etching and measuring bias conditions. The bias for capacitance measurement was set around the minimum conductance point under condition of negligible dissolution current. Since the modulation frequency and its magnitude are also important parameters for C-V measurement, they were optimized against each electrolyte. After profiling, flatness of the etched surface and sharpness around the confined edge region were measured using a "Dektak" moving stylus surface measuring instrument.

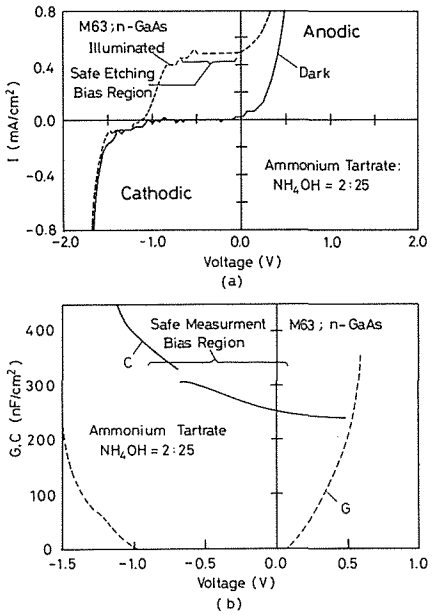


Fig.1 Characteristics of Electrolyte / Semiconductor Schotky Diode; (a) I-V curve under dark and illuminated conditions, (b) C-V, G-V curves.

3. Carrier Concentration Profiling

First, we profiled GaAs and AlGaAs single layers, both n-type and p-type materials, using a small plastic sealing ring with a confining area of 1 mm². All of the electrolytes examined possessed well defined Schottky barrier being appropriate for measuring carrier concentration. The other important factor to be considered for reliable profiling is the etching properties of the electrolyte. Especially, seepage of the electrolyte through the sealing ring incorporates undesirable excess capacitance, and thus large errors are introduced[2]. The situation is schematically shown in Fig. 2 (a), where A_s and A_e indicate the bottom flat surface and excess side area, respectively. The corresponding equivalent

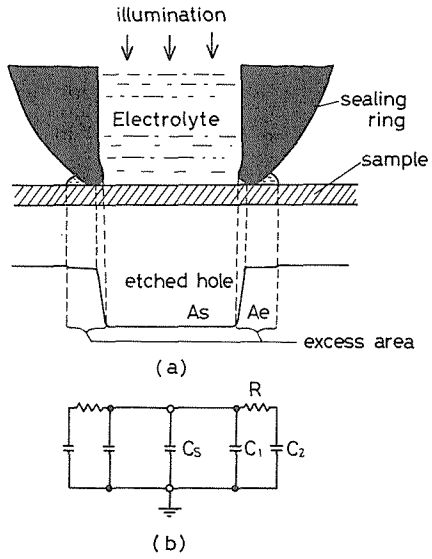


Fig.2 (a) Schematic cross sections of the electrolyte / semiconductor contact zone using a plastic sealing ring, and (b) corresponding ac equivalent circuit.

circuit is also shown in Fig. 2 (b), where C_s denotes the capacitance arising from A_s, and C_1 and C_2 denote the excess capacitances from the circumferential shadow region of the illumination and from the outside of the sealing ring, respectively. C_2 is connected to series resistance, R, due to reduced current conduction under the sealing ring. The profiler can subtract these excess capacitances by considering A_e for the calculation of carrier concentration. This method is one of the practical ways, when the doping density does not change so much throughout the layer.

However, A_e changed from profiling to profiling even for the same electrolytes, and probably may change during the profiling. Moreover, contribution of C_2 depended on the measurement frequency. For these reasons, large A_e should be avoided even for the profiling of uniform single layers. The situation becomes more serious when profiling of high/low-doped multilayers and transition regions between epitaxy and semi-insulating substrate are concerned, since the error of the correction can be comparable to $C_s$of the low-doped region.

Fig. 3 shows the example of carrier concentration profiles obtained by using different electrolytes. Carrier concentration was calculated by subtracting typical $C_1 + C_2$ value against each electrolyte. Except for Se-doped $Al_xGa_{1-x}As$ layers with high compositional factors, x, above about 0.25, most of profiled curves were flat, indicating that uniform doping is achieved throughout the layer. However, in Fig. 3, particular Zn-doped GaAs and Se-doped AlGaAs layers with fluctuating doping density are shown together with an uniformly doped normal layer. All electrolytes examined are able to reflect the variation of carrier density with depth, that is, the p-type GaAs layer is characterized by a small pile-up and deficiency of doping density close to the surface, while periodical ripples of doping

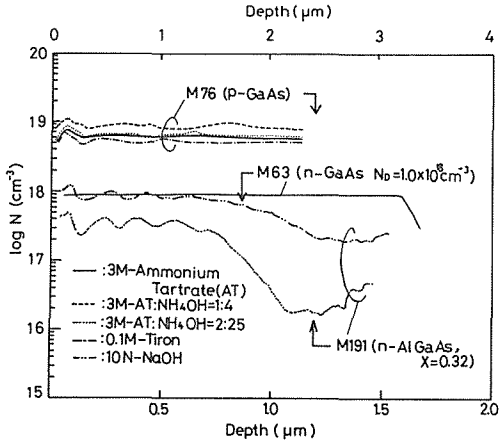


Fig.3 Example of carrier density profiles showing the difference between profiles for different electrolytes.

density for the n-type AlGaAs are seen. However, it is seen that the calculated doping level depends on the electrolyte even after considering the typical $C_1 + C_2$ values. The deviation of carrier concentration sometimes extended over a few hundred percents when a small sealing ring was used. Experimentally, the area corresponding to C_2 was highly dependent on the electrolyte, while the area corresponding to C_1 was not, and high pH solution such as 1N-KOH and buffered 3M-ammonium tartrate solution (pH = 11) tended to give a large fluctuation of A_e as well as large A_e.

Concerning etching properties, flatness of the bottom etching surface must be held, especially for the profiling of the multilayer laser structures and epitaxy/semi-insulating substrate transition regions. 0.1M-Tiron and 3M-ammonium tartrate solutions buffered by NH_4OH (2 : 25) were capable of giving considerably flat and shiny bottom surface, when etching bias was set at proper values. Fig. 4 shows examples of "Dektak" trace of etched hole after profiling of the GaAs layers on semi-insulating substrate. In the figure, (a) - (c) indicate the traces after etching off n-GaAs layers at different bias conditions, that is, (a) ; etched within saturated photocurrent region where dark leakage current is negligible, (b) ; etched under a large reverse biased condition where dark leakage current is no longer negligible, and (c) ; etched under a small biased condition where photocurrent is non-saturated. 0.1M-Tiron was used for the electrolyte. Although the long range flatness (ΔD) seems not to depend on the etching bias, the short range flatness (Δd) is considerably influenced, i.e. defect sensitive etching takes place both in (b) and (c). Etched pits appearing in (b) can be interpleted as the result of enhanced leakage current at the defects, while the raised feature in (c) seems to be due to the shrinkage of photocurrent at the defects, as described in ref. 3. While (d) indicates an example for a p-type GaAs on semi-insulating substrate, showing that the confined circumference is etched deeper than in the center portion. This seems to be attributable to the non-uniform current flow after reaching of the bottom surface to the interface. Note that the bias is set in a forward direction for p-

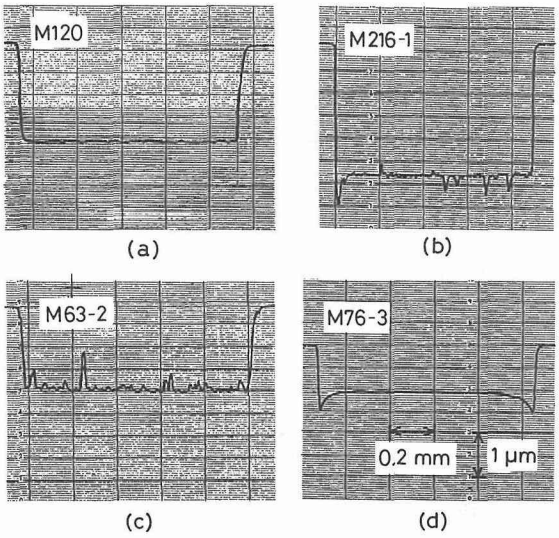


Fig.4 "Dektak" trace of etched hole after the profiling, where the plastic sealing ring was used.

type samples, in contrast to n-type samples, so that the current from the side area remains flowing. For this reason, long range flatness seems to be achieved until the etched surface approaches the substrate. It was found that both short range and long range flatness below $\pm$ 200 Å is obtainable under conditions of appropriate etching bias and etching current density.

Table I summarizes the profiling results of Se-doped GaAs single layers, together with the results of Hall effect measurements and "Dektak" measurements. In the Table, $N_D/N_{D,mean}$ denotes the maximum deviation from mean donor density in the Se-doped CaAs layer except near the epitaxy/substrate interface. It is seen that the uniformity of carrier concentration with depth is quite good in Se-doped GaAs samples. Furthermore, it is known that the etched depth calculated from anodic current is in good agreement with "Dektak" measured depth.

Note that the percent side area, A_e, is typically 8-15% of the total area ($A_s + A_e$) when the small sealing ring and 0.1M-tiron electrolyte are used.

Table 1. Summary of Electrochemical Profile for Se-doped GaAs Layers

Sample	Hall Effect	Microscope	Electrochemical Profiler			"Dektak" Profiler		
	N_D (cm^{-3})	Thickness (μm)	N_D (cm^{-3})	Etched Depth (μm)	$\Delta N_D / N_{D,meam}$	Depth (μm)	$\Delta d(\mu m)/\Delta D(\mu m)$	Side Area (%)
M43	1.22×10^{18}	3.1	1.3×10^{18}	2.98	1.20	2.7	$\pm$0.03/0.1	13
M44	2.56×10^{18}	3.0	2.3×10^{18}	3.04	1.09	2.9	$\pm$0.03/0.05	8
M120	7.3×10^{17}	2.33	9.0×10^{17}	2.69	1.04	2.5	$\pm$0.02/0.1	14
M133	2.93×10^{18}	2.74	3.2×10^{18}	2.56	1.05	2.2	$\pm$0.35/0.1	12
M134	5.76×10^{18}	2.24	6.0×10^{18}	2.65	1.12	2.1	$\pm$0.02/0.05	15

Similarly, uniformity of Zn-doped GaAs and AlGaAs were also confirmed by the profiler. Regarding Se-doped AlGaAs, uniform doping was confirmed up to $x = 0.2$. However, the capacitance dispersion with frequency became larger with increasing x for $x > 0.2$; besides, profiled doping density was depleted near the epitaxy/substrate interface, as was shown in Fig. 3. The capacitance dispersion is attributed to the deep levels responding to low frequency, that is, it is well known that the doping of donor impurities into AlGaAs results in the formation of DX centers.

It was found that the average free carrier concentration measured by Hall effect method decreased with increase in the Al composition, while the impurity concentration measured by the profiler was not strongly depended on it within the uniform region. Experimentally, the concentration ratio of the impurity to free carrier was 1.3 at $x = 0.18$, 3.7 at $x = 0.25$ and 12-13 at $x = 0.32$.

The reason for the depleted impurity density near the interface is not known precisely at present. However, the existence of heterojunctions, namely, conduction band discontinuity[4], a memory effect of Se dopant, and compensating shallow acceptor seem to be involved.

As mentioned previously, profiling of high/low-doped multilayers and epitaxy/semi-insulating transition regions becomes difficult, when a small sealing ring is used for the definition of electrolyte/semiconductor contact area. For this reason, thick photoresist or light-tight wax combined with the large plastic sealing ring was normally used for accurate profiling. The situation is schematically shown in Fig. 5 with the corresponding equivalent circuit. Since the thickness of photoresist exceeded several μm (over several tens μm for light-tight wax) and the diameter of the sealing ring was about 3 mm, its capacitance contacted to the electrolyte was neqligible compared to the Schottky capacitance, C_s,

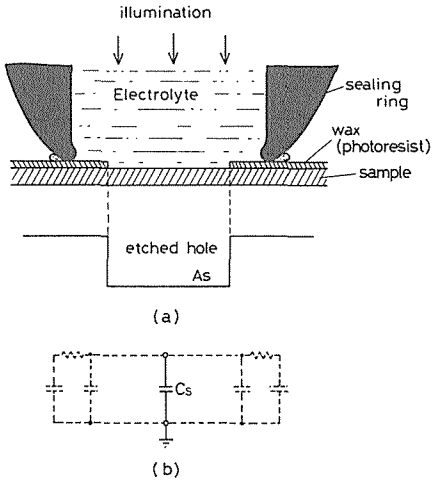


Fig.5 (a) Schematic cross sections of the electrolyte / semiconductor contact zone using a thick photoresist combined with the large sealing ring, and (b) corresponding ac equivalent circuit.

within the interesting range of the carrier concentration, i.e. down to $1x10^{15}$ cm^{-3}. The seepage of the electrolyte through the sealing ring becomes no longer a problem. Moreover, the circumference shadow region previously observed, as shown in Fig. 2(a), is completely eliminated, so that the excess capacitance arising from the non-flat side area is considerably reduced. The example of "Dektak" trace of etched hole is shown in Fig. 6, where 0.1M-tiron was used as the electrolyte. Note the sharpness of the etched wall. The side area can be estimated to be ~3 % of the total area, being independent of the electrolyte examined, which is 1/5 - 1/3 compared with that using the plastic sealing ring.

Fig. 7 shows the example of carrier concentration profiles of a Se-doped GaAs layer on semi-insulating substrate, where the difference of profiled curves between two confining methods is demonstrated. When black wax is used for the definition of the contact area, the profiled carrier concentration usually dropped to 2.5 - 3 orders magndtude smaller value than the uniformly doped region, as indicated by a bold line, provided that flat etching of the bottom surface is achieved until epitaxy/substrate interface. The result should be compared to the profiled curve obtained by using the sealing ring; typically, a 1 - 1.5 order drop is observed. In order to check the validity of the former profiled curve, metal Schottky barriers were formed on chemically etched steps near the epitaxy/sub-

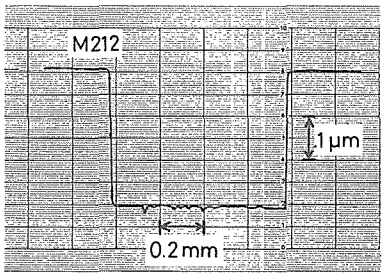


Fig.6 "Dektak" trace of etched hole after the profiling, where light-tight wax was used for the contact definition.

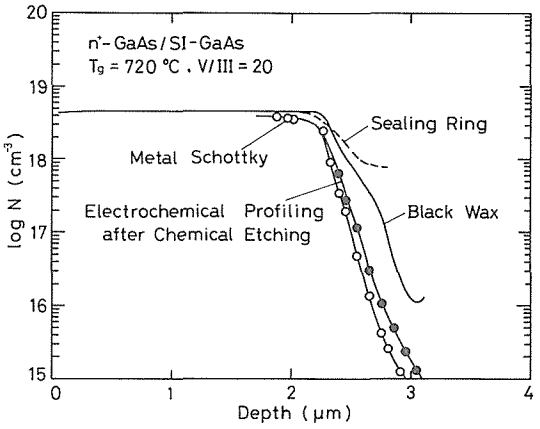


Fig.7 Carrier concentration profiling near Se-doped GaAs / semi-insulating substrate interface.

strate interface. The above profiling method using black wax was also employed after removal of thick high-doped layer from the surface, to reduce the capacitance contribution from the excess side area further. The results are shown in Fig. 7, where lines with open circles and closed circles indicate the metal Schottky profile and the electrochemical profile after etching off the thick n^+-layer, respectively. It may be seen that the metal Schottky profile and the electrochemical profile are reasonably in agreement, and that the original curve profiled to the sample having thick n^+-layer is close to those curves in shape, although the drop of the curve is limited to about 2.5 orders. The shift between the curves seems due to both experimental error and lateral difference in the layer thickness. It should be also noted that the carrier concentration profiling held down to 10^{14} cm^{-3} range become possible when thick n^+-layer is removed and black wax is used. It was found that the effect of series resistance during capacitance measurement is negligible until carrier concentration approaches the middle of 10^{14} cm^{-3} range. From the above profilings, it was found that the transition width between Se-doped GaAs and semi-insulating substrate became narrower with increasing AsH_3/TMG ratio. The transition width of 0.2 μm, being assessed as a 2 order drop in carrier concentration, was met under normal growth conditions, that is, T_g = 720°C and AsH_3/TMG = 20. It seems that the transition layer belongs to semi-insulating substrate, originally, because the thickness of the uniformly doped region was almost independent of AsH_3/TMG ratio, as expected, while the thickness of the transition layer strongly depended on it, under the condition of constant growth time.

An example of carrier concentration profile for a high/lowdoped multilayer is shown in Fig. 8.

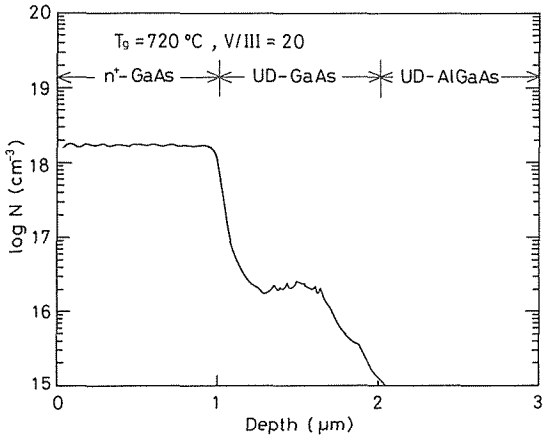


Fig.8 Carrier concentration profile of a high/low-doped GaAs/AlGaAs multilayer.

The epitaxy consists of three layers, that is, Se-doped GaAs (1μm), UD-GaAs (1μm) and UD-AlGaAs buffer (1μm, x = 0.3) from the surface. The transition width between n^+-GaAs and UD-GaAs assessed by the one decade drop in carrier concentration is about 600 Å, as seen from Fig. 8. The resolution of the profiler is less than the above value of 600 Å when Debye Length of the doped layer is considered. Similar curves were obtained for the same structures but with different AsH_3/TMG ratio, and the transition width seems to be less dependent on AsH_3/TMG ratio, in contrast to the n^+-GaAs/semi-insulating substrate transition. Thus, quite reasonable profiles can be obtained again for high/low-doped multilayers by using a photoresist or light-tight wax.

4. Composition Profiling

The compositional factor, x, of GaAs/$Al_xGa_{1-x}As$ multilayers is also of great interest in laser operations. For convenient and rapid evaluation of the compositional factor, the open-circuit photovoltage spectrum of the electrolyte/semiconductor Schottky barrier was measured by interrupting the profiling of carrier concentration. This method, which is based on the fundamental light absorption by the generation of electron-hole pairs, was also reported Wakefield et al.[5]. Here, the validity of the method is examined by comparing with photoluminescence (PL) data.

Fig. 9 shows the block diagram of the constructed photovoltage measurement system. Monochromatic light obtained from a tungsten lamp and a monochrometer is collimated and chopped with a frequency of 12 Hz, in order to avoid the slow drift arising from a relaxation of the Helmholtz layer, then the light is guided into the electrochemical cell. The photovoltage signal from the sample is amplified by a lock-in amplifier and recorded on a X-Y chart. It should be noted that the dissolution of the sample is negligible during the photovoltage measurement.

Fig. 10(a) shows photovoltage spectra of n-type $Al_xGa_{1-x}As$ single layers with different Al composition, which are normarized by the maximum photovoltage, $V_{ph,max}$. No correction against incident photon numbers is made for the sake of rapid evaluation of x ; Besides, intrinsic absorption of the direct transitions is proportional to $(hc/\lambda\text{-}E_g)^{1/2}$. However, here, the Al composition in $Al_xGa_{1-x}As$ layer was calculated from the mid-point energy of the spectrum near the band edge region, using the following empirical equation[6] :

$$E_g(Al_xGa_{1-x}As) - E_g(GaAs) = 1.226x + 0.266x^2 \quad (x < 0.37) \tag{4}$$

Fig. 10(b) shows the comparison of Al mole fraction (%Al) determined from the photovoltage measurement to that from photoluminescence measurement, where the peak energy of PL intensity was assigned to the band gap energy, since the near-gap emission usually peaks very close to the band gap. It is seen that the correlation between two methods is fairly good within the error of $\pm$ a few %, as far as direct transitions are concerned ($x < 0.37$).

The example of the carrier concentration profile together with the corresponding set

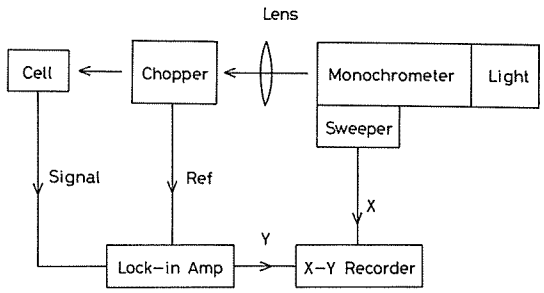
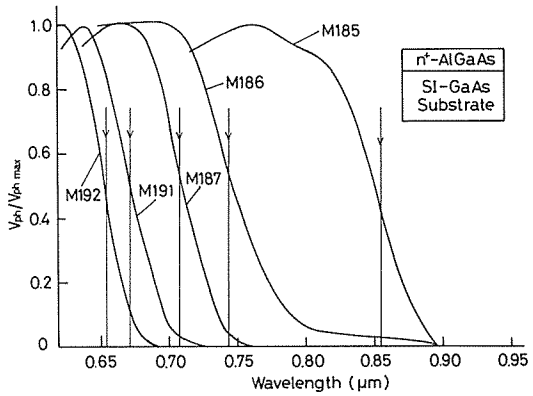
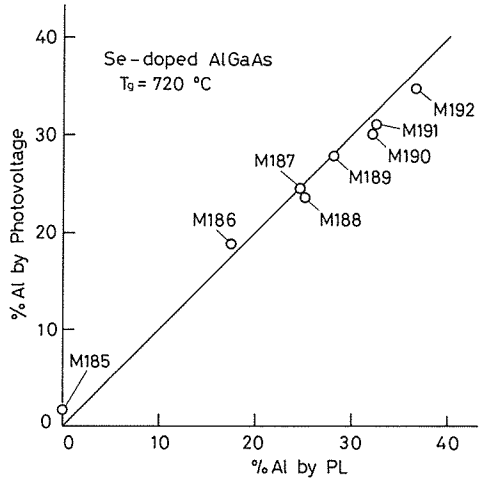


Fig.9 Block diagram of the photovoltage measurement system.



(a)



(b)

Fig.10 (a) Normarized photovoltage spectrum of $Al_xGa_{1-x}As$ layers, and (b) Comparison of %Al from photovoltage spectrum to that from photoluminescence measurements.

of the photovoltage spectra is shown in Fig. 11, which is obtained from a multilayer structure having p^+-AlGaAs ($1 - 2x10^{18}cm^{-3}$)/undoped GaAs ($10^{16}cm^{-3}$ range)/n^+-AlGaAs ($5x10^{17}cm^{-3}$ range)/n^+-GaAs ($1 - 2x10^{18}cm^{-3}$) layers on n^+-GaAs substrate.

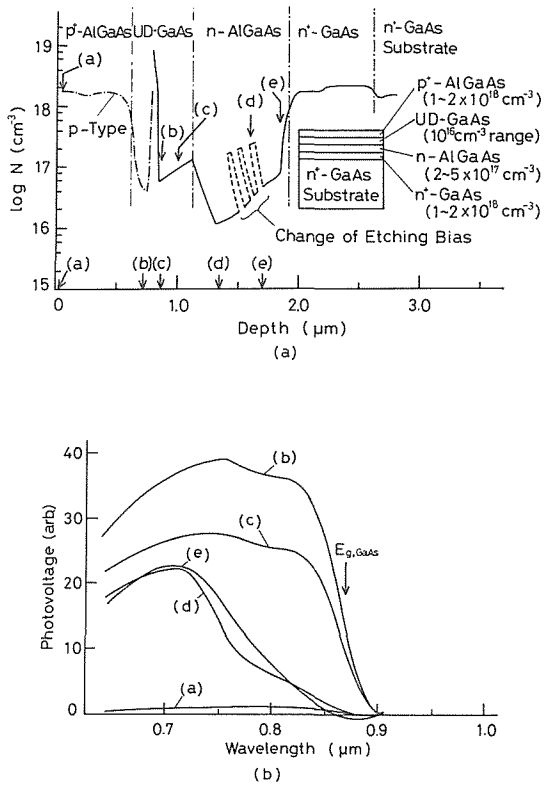


Fig.11 (a) Carrier concentration profile, and (b) corresponding set of the photovoltage spectrum.

During the profiling of p-type region, the anodic current was supplied by biasing the sample to a forward direction in the dark, while the dissolution current of the n-type regions was supplied by illuminating the sample as described previously. When the p-n junction is approached, the dissolution current decreases considerably, provided that the etching bias is set at an appropriate value. Regarding the measurement of the capacitance, after the depletion layer of p-type region reaches the p-n junction, the profiling becomes difficult at least until the etching progresses through the junction owing to the complicated polarization of the semiconductor, which is seen in the profiled curve. Then the measurement conditions were changed to be appropriate for n-type material. Each layer is clearly distinguishable, although the carrier concentration in the n^+-AlGaAs layer is much smaller as compared with expected carrier concentration from Hall effect measurement done on similarly grown thick n^+-AlGaAs single layers. The phenomenon seems partly due to the incorporation of deep traps and shallow acceptors in this region,

and partly due to the the conduction band discontinuity, as described previously. The profiling in this region was highly sensitive to the etching bias, that is, the etching under a large reverse biased condition gave a larger impurity concentration, as shown by dashed lines, which implies the existence of deep traps comparable or greater than the free carrier concentration.

Regarding the photovoltage spectrum, the letters on the profiled curve indicate the measurement points of the spectrum. Since they are different from etching depth, corresponding etching depths are also marked on the depth axis. The photovoltage during the p-type surface condition gave opposite signs to the expected ones from the Schottky barrier, namely, the same polarity as for n-type surface. The reason for this can be explained by the competition between photovoltages arising from the p-type Schottky barrier and from inner p-n junction, since a photovoltage with normal sign was usually observed against thick p-type single layers. Except for p-type region, the change of the spectrum with etching depth is clear, as shown in Fig. 11(b). The Al composition of n-type AlGaAs layer is estimated to be 0.20. The value is reasonably in agreement with PL data of 0.23 obtained from n-type AlGaAs single layers grown under the same conditions.

5. Conclusions

In conclusion, an automatic carrier concentration depth profiling system is used to assess MOCVD grown GaAs and AlGaAs single layers, and GaAs/AlGaAs multilayers for laser diodes. Reliable profiling with considerably reduced influence from the excess side area has been demonstrated through the use of a thick photoresist or a light-tight black wax with a large plastic sealing ring. The area below 1 mm^2 is sufficient for the profiling, so that the method is highly effective to reduce material consumption. With this confining method, uniformity of p-type and n-type GaAs, and AlGaAs layers was confirmed except n-type AlGaAs layers with Al composition, x, larger than 0.2. Furthermore, profiling of high/low-doped multilayers and the transition regions between epitaxy/semi-insulating substrate becomes possible. The validity of determining Al composition in $Al_xGa_{1-x}As$ layers by the photovoltage spectroscopy measurement has been also studied.

The Al composition determined from photovoltage measurement is consistent with the photoluminescence result. Finally, the example of simultaneous profiling of the carrier concentration and Al composition for a GaAs/AlGaAs multilayer was given.

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References

1) T. Ambridge and M. Faktor, Inst. Phys. Conf. Ser., no. 24 (1975) 320.
2) T. Ambridge, J.L. Stevenson and R.M. Redstall, J. Electrochem. Soc., 127 (1980) 222.
3) M.M. Faktor and J.L. Stevenson, J. Electrochem. Soc., 125 (1978) 621.
4) M.O. Watanabe, J. Yoshida, M. Mashita, T. Nakanishi and A. Hojo, J. Appl. Phys., 57 (1985) 5340.
5) B. Wakefield, J.L. Stevenson, R.M. Redstall and T. Ambridge, Appl. Phys. Lett., 35 (1979) 347.
6) H. Kressel and J.K. Butler, Semiconductor Lasers and Heterojunction LEDs, Academic Press, 1978.