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Optimizing HBr-Br_2-H_2O Etchants to Form Low Defect Regrowth Interfaces for Highly Reliable InGaAsP/InP Buried-Heterostructure Lasers

K. Shinoda,[z] A. Taike, H. Sato, and H. Uchiyama

Hitachi, Limited, Central Research Laboratory, Kokubunji, Tokyo 185-8601, Japan

We have obtained a tenfold improvement in the reliability of InGaAsP/InP buried heterostructure laser diodes having a dry-etched mesa structure by optimizing the composition of a HBr-Br_2-H_2O etchant to produce smooth mesa sidewalls, thus reducing the number of defects at regrowth interfaces. The optimal etchant, which has a composition in the range from 0.30 M HBr/0.022 M Br_2 to 0.50 M HBr/0.020 M Br_2, etches both the InP($\bar{1}10$) cladding layers and the InGaAsP($\bar{1}10$) multi-quantum-well active layer at the same rate. We propose a simple model of the HBr-Br_2-H_2O etching process that is consistent with the observed etching characteristics. We found that the etching rate was controlled by the diffusion of Br_2 molecules, which act as oxidizing agents.
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To achieve highly reliable operation of buried-heterostructure laser diodes (BHLDs), which are vital components of optical transmission systems,[1,2] we must reduce the number of defects at regrowth interfaces around the mesa structures formed by dry etching followed by wet chemical etching. However, conventional wet chemical etching produces faceted mesa sidewalls because of the difference in etching rate between InP cladding layers and the InGaAsP multi-quantum-well (MQW) active layer as well as between various different crystal planes.[3] These faceted mesa sidewalls disrupt the uniformity of growth, so defects are formed during epitaxial regrowth. Therefore, the lasing characteristics of BHLDs gradually worsen during operation as the number of defects at the regrowth interfaces increases. Finding a wet chemical etchant that produces smooth mesa sidewalls is thus very important.

In this paper, we report on an investigation of wet chemical etchants used for etching dry-etched mesa structures. We started by examining the mechanisms by which various etchants act on InP/InGaAsP materials and chose HBr-Br_2-H_2O solutions as the most suitable etchants for obtaining smooth mesa sidewalls. We found that the etching characteristics depended on the solution's composition, so we were able to find the best HBr-Br_2-H_2O etchant composition for producing smooth mesa sidewalls. We also propose a simple model of this etching process; its predictions agree well with experimental results. Although a HBr-Br_2-H_2O etchant was used to etch the InGaAsP/InP mesa structure in an earlier study, the sidewalls of the resulting mesa were rough and there was a bump on each side of the MQW active layer.[3] The present study thus represents the first time that smooth mesa sidewalls have been formed by using a HBr-Br_2-H_2O etchant that was compositionally optimized to etch InP and InGaAsP at the same rate. This etchant suppressed the generation of defects at the regrowth interfaces and improved the reliability of the BHLDs.

Experimental

Choice of etchant system.—Wet-etching profiles are strongly affected by whether the dissolution rate is diffusion controlled or kinetically controlled. Whereas kinetically controlled dissolution tends to produce faceted surfaces because the dissolution rate depends on the crystal plane and the composition of the material being etched, diffusion-controlled dissolution is more likely to produce smooth surfaces. This is because the rate-determining process in diffusion-controlled etching is the arrival of etchants at solid surfaces, so any differences in reaction rate that may exist for various crystal planes and compositions do not affect the etching rate. Therefore, diffusion-controlled etchants are preferable for producing smooth mesa profiles.

Among the many systems for etching InP/InGaAsP that have been presented to date,[3,4] ones that contain bromine tend to be diffusion controlled. We therefore chose to examine HBr-H_2O_2-H_2O and HBr-Br_2-H_2O. These are composed of an acid (HBr), an oxidizing agent (H_2O_2 or Br_2), and water. Thus, their etching processes are considered to consist of surface oxidation by the oxidizing agent, followed by the dissolution of the oxides in the presence of the oxonium ions produced by acids diluted in water.

We examined the relative stability of the two etchants by evaluating their etching rates for InP(001) as a function of time after the solution was mixed (Fig. 1). Here the etching rate represents a rough estimate of the initial rate of etching. In this paper, it was calculated by measuring the etched depth of the samples after they had been etched in the solution for 2 min. It is difficult to obtain a precise value for diffusion-limited etching because the etched depth does not increase linearly with time.

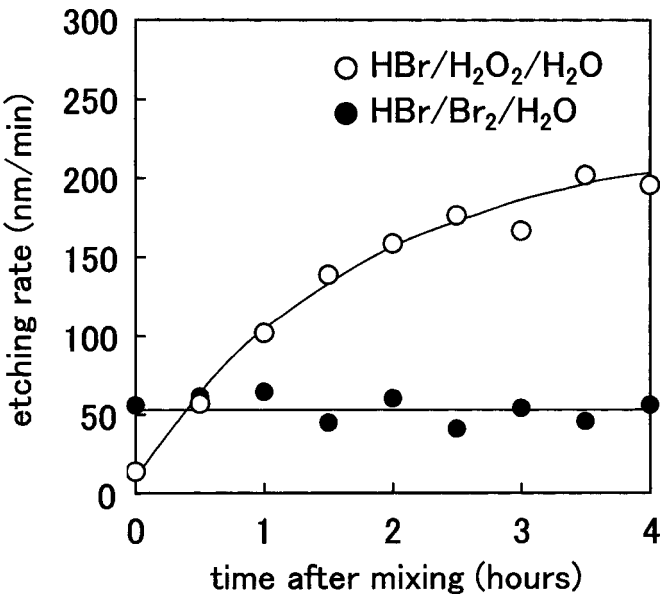

Figure 1. Etching rate of InP(001) *vs.* time after mixing each solution: (○) HBr-H_2O_2-H_2O etchant (0.55 M HBr, 0.19 M H_2O_2), (●) HBr-Br_2-H_2O etchant (1.5 M HBr, 0.01 M Br_2).

[z] E-mail: shinoda@crl.hitachi.co.jp

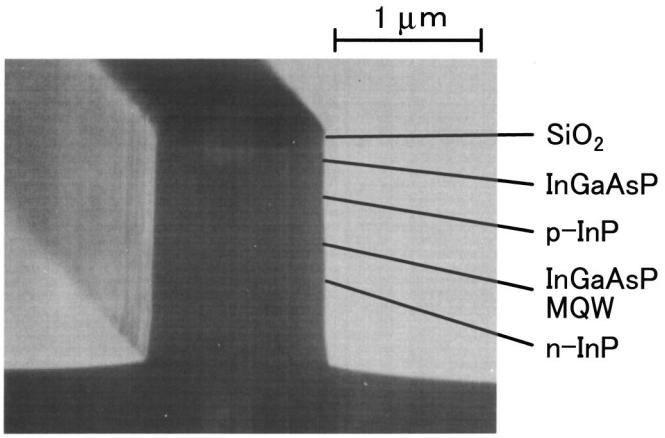

Figure 2. SEM cross-sectional image of a dry-etched mesa.

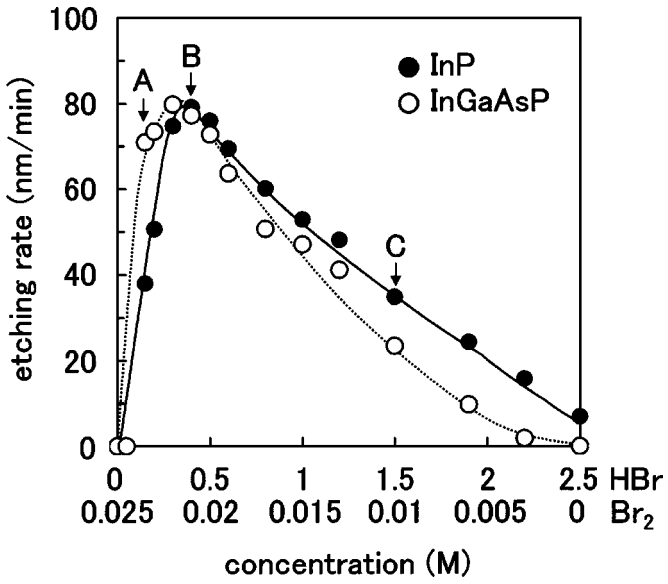

Figure 3. Etching rates of (●) InP($\bar{1}\bar{1}0$) and (○) InGaAsP($\bar{1}\bar{1}0$) as a function of HBr and Br_2 concentrations.

The etching rate in HBr-H_2O_2-H_2O was negligible immediately after mixing but increased substantially over time. The explanation for this is as follows. H_2O_2 did not act as an oxidizing agent because HBr-H_2O_2-H_2O hardly etched InP. As time proceeded, however, H_2O_2 oxidized Br^- ions to produce Br_2 which did act as an oxidizing agent. This is because the standard redox potential for H_2O_2 (1.763 V) is higher than that for Br^- (1.087 V).[5] This explanation was confirmed by the observed color of the solution, which gradually changed from colorless to red, the color of bromine. Therefore, we do not consider HBr-H_2O_2-H_2O to have good reproducibility in etching of InP and InGaAsP. Consequently, hereafter, we only discuss the HBr-Br_2-H_2O etchant system.

Procedure.—The dependence of the etching rate of InP($\bar{1}\bar{1}0$) and InGaAsP($\bar{1}\bar{1}0$) on the composition of the HBr-Br_2-H_2O solution was investigated by using InGaAsP/InP multilayered structures grown by metallorganic chemical vapor deposition (MOCVD) on Sn-doped InP(001) wafers. The multilayered structure consisted of an InGaAsP MQW active layer (λ_g = 1.3 μm), a p-InP cladding layer, and a p-InGaAsP capping layer. 1.5 μm high mesas were fabricated by reactive ion etching with a $CH_4/H_2/O_2$ gas mixture through SiO_2 stripe masks arranged in the [110] direction. Figure 2 shows a cross-sectional image of the dry etching profile observed by scanning electron microscopy (SEM). HBr and Br_2 concentrations were varied while keeping [HBr] + 100[Br_2] = 2.5 M. Wet chemical etching was carried out at room temperature without stirring under ambient illumination. The etched depths perpendicular to the vertical mesa were then measured by SEM.

Epitaxial regrowth was carried out by MOCVD. Thin layers of InP were grown over the mesas so we could observe their structures. SEM and transmission electron microscopy (TEM) were used to characterize the regrowth profiles and defects at the interfaces. BHLDs fabricated using various HBr-Br_2-H_2O etchants were lifetime tested by operating them at a constant optical power output of 10 mW at 85°C.

Results and Discussion

Figure 3 shows the etching rates of InP($\bar{1}\bar{1}0$) and $In_{0.76}Ga_{0.24}As_{0.55}P_{0.45}$($\bar{1}\bar{1}0$) ($\lambda_g$ = 1.3 μm) as a function of HBr-Br_2-H_2O concentration. Both rates showed a similar dependence on composition. Neither material dissolved in aqueous Br_2. The rates increased with HBr concentration and reached their respective maxima at HBr concentrations of about 0.4 M, and then decreased with a further increase in HBr concentration, which corresponds to a decrease in Br_2 concentration. InP and InGaAsP were etched at almost the same rates in the concentration range from 0.30 M HBr/0.022 M Br_2 to 0.50 M HBr/0.020 M Br_2. The morphology of the etched surfaces was mirrorlike in most cases. However, etchants with very little HBr (from 0.025 M Br_2 to 0.05 M HBr/0.0245 M Br_2) produced rough surfaces. We also found that the etching rates by such low HBr etchants were not reproducible. These findings provide strong evidence that the dissolution of InP and InGaAsP in HBr-Br_2-H_2O solutions is mainly due to the dissolution of oxides, which requires both oxidizing agents and acids. The roughness produced by etchants with very little HBr may be due to the masking effects of residual oxide that remains on the surface because of insufficient acidity. It is clear that both materials hardly dissolved in either aqueous Br_2 or aqueous HBr. However, InP would be etched substantially if the acidity of the solution were much higher than in our experiments.[6] This is because $InPO_4$, which is the most thermodynamically stable solid phase in the InP-H_2O system, is no longer stable in a strongly acidic solution and tends to be reduced to produce In^{3+} plus H_3PO_4, In^{3+} plus H_3PO_3, or In^{3+} plus PH_3, as depicted in the potential-*p*H diagram provided by Hsieh and Shih.[7] This explanation is consistent with the observation that InP was etched a little in aqueous HBr, which is much more acidic than aqueous Br_2. Profiles of the mesa walls etched by the particular solutions labeled A-C in Fig. 3 are discussed later.

Figure 4 shows the temperature dependence of the etching rate of InP(001) by 0.50 M HBr/0.020 M Br_2, which etches InP and InGaAsP at the same rate. The increase in rate on a logarithmic scale *vs.* temperature was insignificant and the activation energy was 0.14 eV. This low activation energy indicates that the etching reaction was diffusion controlled. If the etching rate had been controlled by the chemical reaction at the surfaces, the activation energy would have been much greater. Etching reactions with an activation energy greater than 0.4 eV are tentatively classified as kinetically controlled. Furthermore, the etched depth of about 80 nm observed after exposure for 1 min at 25°C leads us to think that the diffusing etchant species may have been Br_2 molecules for the following reasons. Since the diffusion coefficient D of any chemical species in aqueous solutions at room temperature is of the order of 1×10^{-9} m^2/s,[8,9] the diffusion length $\sqrt{4Dt}$ of the etchants over t = 1 min is estimated to be around 500 μm. Thus, roughly speaking, only the etchant within 500 μm of the solid surfaces can reach

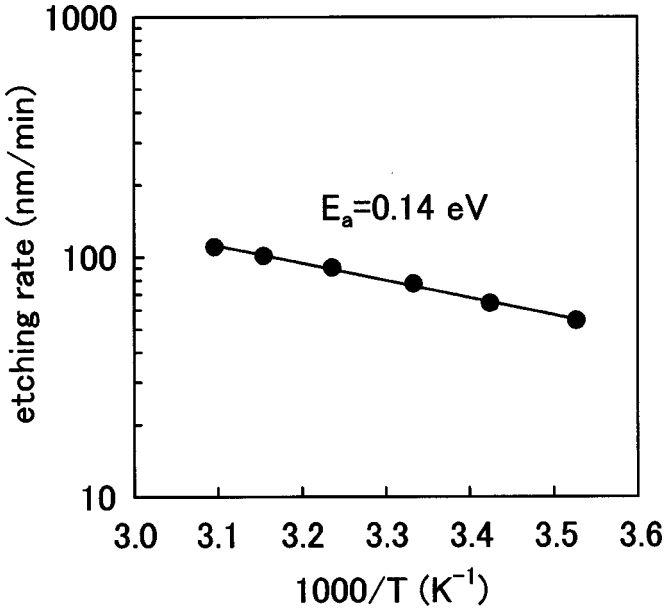

Figure 4. Temperature dependence of etching rate of InP(001).

them. Earlier studies revealed that $InPO_4$ is the dominant oxidized state of InP after various treatments.[7,10-13] Thus, assuming that the oxidized state of InP is $InPO_4$, the redox reactions may be expressed as[5,7]

$$InPO_4 + 8H^+ + 8e^- = InP + 4H_2O \quad [1]$$

$$4Br_2 + 8e^- = 8Br^- \quad [2]$$

Since the standard redox potential of Reaction 2 (1.087 V) is higher than that of Reaction 1 (−0.385 V), Br_2 can oxidize InP. Thus, these redox reactions can be merged into a single reaction

$$InP + 4Br_2 + 4H_2O \rightarrow InPO_4 + 8Br^- + 8H^+ \quad [3]$$

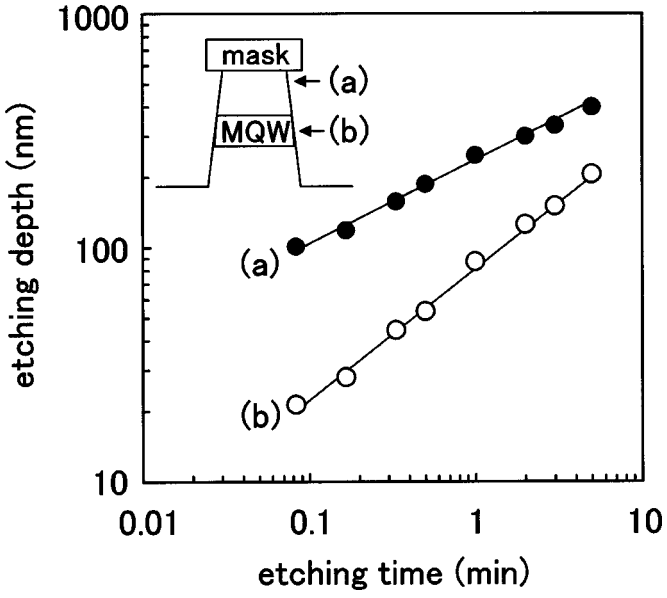

Figure 5. Depth of side etching at different positions as a function of etching time: (a) in the vicinity of the mask edge and (b) on the MQW active layer.

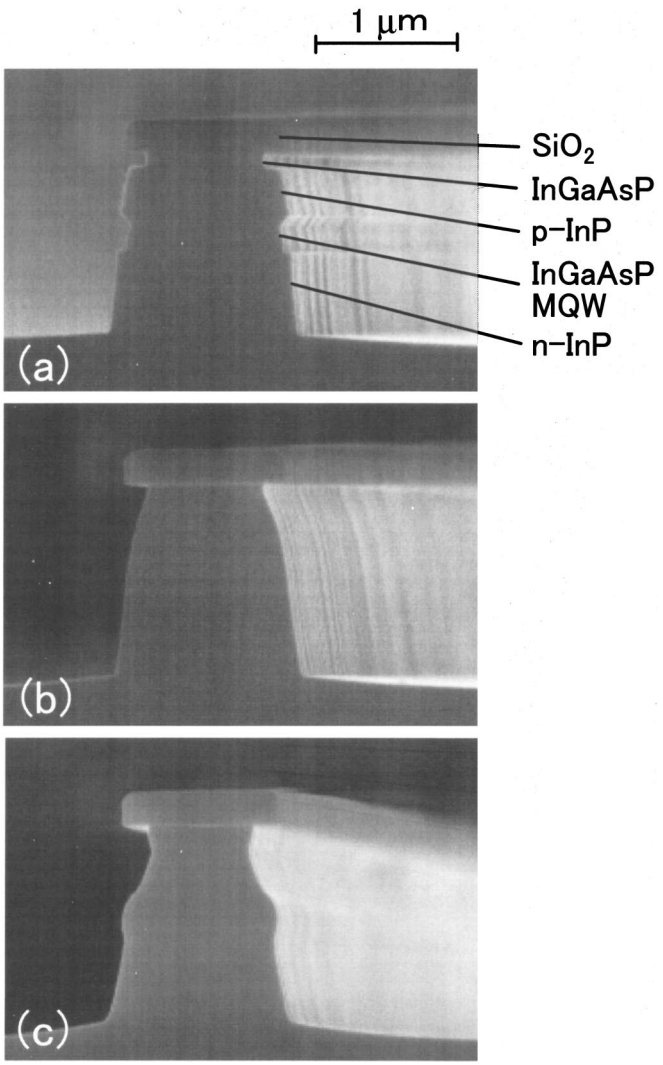

Figure 6. SEM cross sections of wall profiles formed by (a) etchant A, (b) etchant B, and (c) etchant C.

Therefore, four Br_2 molecules are consumed in etching one InP molecule. The depth of etching (δ) by a purely diffusion-controlled etchant may be approximated by[14]

$$\delta = \frac{CM\sqrt{4Dt}}{N\rho} \quad [4]$$

where C is the concentration of the etchant, M is the mass of one molecule of the solid, N is the number of etchant molecules needed to remove one molecule from the solid, and ρ is the density of the solid. Thus, the etching depth of InP produced by exposure to 0.5 M HBr/0.02 M Br_2 for 1 min is estimated to be about 80 nm. This estimate agrees well with the etching depths that we observed. On the other hand, if we consider that the rate-determining etchants are Br^- ions and assume that three Br^- ions are used in etching one InP molecule, then the etching depth can be estimated as 2.5 μm, which is much greater than the observed depth. The large difference is mainly due to the difference in the concentration of the etchant species (0.5 M for HBr and 0.02 M for Br_2). This argument indicates that the diffusion of Br_2 molecules determines the etching rate.

In such diffusion-controlled etching, the presence of a mask is known to enhance etching in its vicinity. The etching rates are thus largest close to the mask edges and the distance from them has a strong effect on the depth of side etching.[14,15] This phenomenon

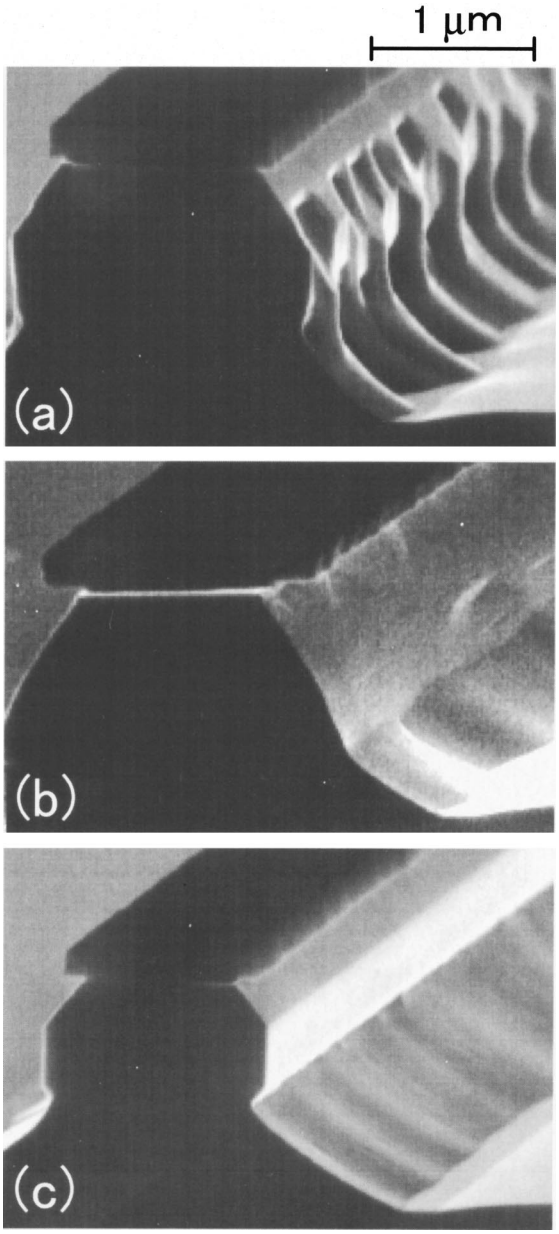

Figure 7. SEM cross sections of regrowth profiles formed using (a) etchant A, (b) etchant B, and (c) etchant C.

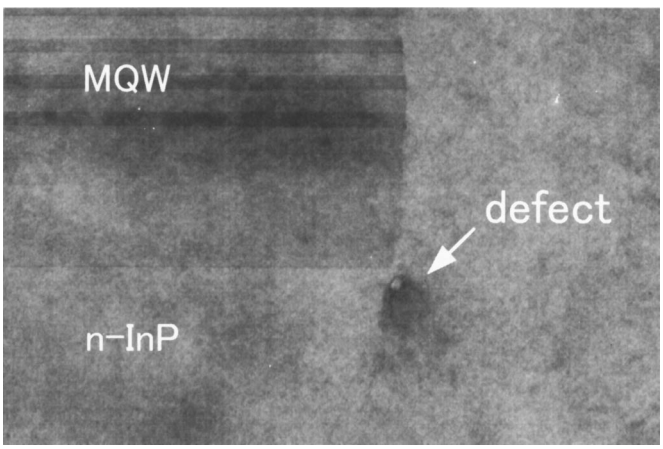

Figure 8. TEM image of an interface produced using etchant C, which causes rough sidewalls.

might cause uneven sidewalls. Figure 5 plots the depth of side etching immediately below the mask and at the MQW active layer. The slope of curve a is 0.35 (mask edge) while that of curve b is 0.59 (MQW active layer). Both slopes are reasonably close to the figure of 0.5 that would be expected for purely diffusion-controlled etching. This $t^{1/2}$ dependence is expected for purely diffusion-controlled etching because only that portion of the etchant that is within the diffusion length $\sqrt{4Dt}$ can reach the solid surface and etch the material. It is also clear, however, that etching at the mask edge shows a much weaker time dependence than etching of the MQW active layer. This tendency is consistent with the mathematical model of diffusion-controlled etching with convection that was presented by Kuiken *et al.*,[14] who obtained a $t^{2/3}$ dependence at the mask edges and a t dependence at points far from them. The weaker time dependence is because there is a greater supply of fresh etchants in the vicinity of the mask. The lack of forced convection led to our results having a rather weaker time dependence than the results in the literature. The difference between the slopes of etched depth *vs.* time in Fig. 5 was found to cause rough sidewalls when the etching time was short, because of the large difference, at the beginning of etching, between the rates for the regions close to the mask edge and for the MQW active layer. However, the difference between the etching depths became less and less as time passed. Longer etching times are thus preferable from the viewpoint of producing smooth mesa sidewalls unless they cause the widths of the remaining mesa structures to become narrower than designed values.

On the basis of these findings, we tested several etchants on the dry-etched mesa structure. SEM cross sections of the mesa profiles produced by etchants of various compositions are shown in Fig. 6. The etching period was 1 min in each case. The mesa shape produced by the etchant with 0.15 M HBr/0.024 M Br_2 (etchant A) had recesses on each side of the MQW layer. This is because the etching rate of InGaAsP in etchant A was faster than that of InP as shown in Fig. 3. In contrast, the mesa shape produced by 1.5 M HBr/0.01 M Br_2 (etchant C) had a bump on each side of the MQW layer because the etching rate of InGaAsP in etchant C was slower than that of InP. The mesa profile produced by using the etchant with 0.5 M HBr/0.02 M Br_2 (etchant B) had smooth sidewalls because it etched the InP layers and InGaAsP layers at the same rate.

SEM images of regrowth profiles around mesas formed by using these three HBr-Br_2-H_2O solutions are shown in Fig. 7. Etchant B produced high quality regrowth interfaces with uniform growth around the mesa. Etchants A and C, on the other hand, formed nonuniform ones. When etchant A, which produced recesses in the MQW layer, was used, the regrowth profile became very rough because of the difference in growth rate from facet to facet of the sidewalls. When etchant C, which produced bumps at the side of the MQW layer, was used, (111)A planes appeared at the lower edges of the bumps on the side of the MQW active layer. The (111)A planes met curved growth faces like (11n) on the lower parts of the mesa sidewalls as they grew. Thus, some defects were formed in the vicinity of the lower edges of the bumps, as shown in the TEM image in Fig. 8.

Figure 9 shows the results of lifetime testing of BHLDs fabricated using etchants B and C. The change in operating currents, $\Delta I_{op}/I_{op}$, for BHLDs with smooth sidewalls fabricated using etchant B was 0.37% (from 0 to 2100 h at a constant 10 mW optical power output at 85°C), while the corresponding figure for BHLDs with rough sidewalls fabricated using etchant C was 3.0% on average. The change in driving currents was obtained by averaging over five samples for each type of BHLD. We thus conclude that smoother etching profiles improve the reliability of the BHLDs.

Conclusions

We investigated the etching characteristics of InGaAsP/InP mesa structures in various HBr-Br_2-H_2O etchants. Our observations revealed an optimal concentration in the range from 0.30 M HBr/0.022 M Br_2 to 0.50 M HBr/0.020 M Br_2 that etches the InP($\bar{1}10$)

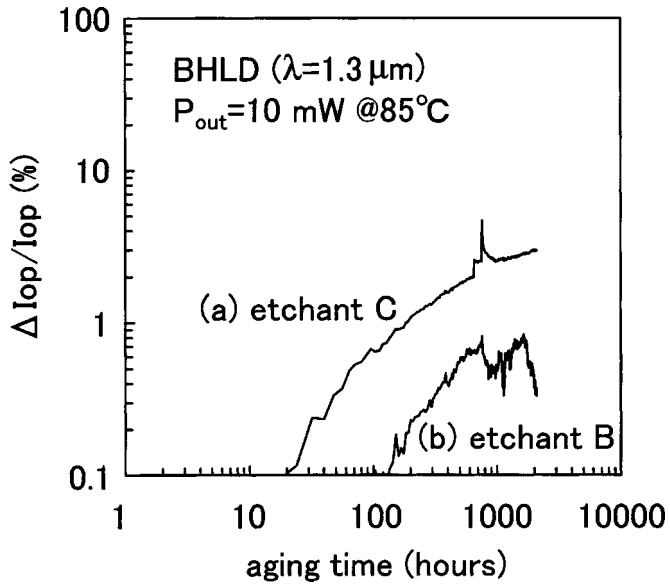

Figure 9. Lifetime-test results: BHLDs with mesa structures formed using (a) etchant C and (b) the optimal etchant B. (The BHLDs produced 10 mW of output power at 85°C.)

and InGaAsP($\bar{1}10$) layers at the same rate. The etching mechanism is diffusion-controlled with an activation energy of 0.14 eV. We proposed a simple model of the etching process that can successfully explain the observed etching characteristics. The etching rate was found to be controlled by the diffusion of the Br_2 molecules, which act as oxidizing agents. High-quality regrowth interfaces with fewer defects were formed on mesa sidewalls treated with the optimal etchant. The processing described in this paper results in a great improvement in the reliability of BHLDs.

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