Improvement of MOCVD Growth Technique Using CBr_4

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ABSTRACT *In-situ* etching of compound semiconductor and selective epitaxial growth of an Al-containing material were realized in a metalorganic chemical vapor deposition (MOCVD) reactor using carbon tetrabromide (CBr_4). *In-situ* etching depended on the content of the compound semiconductor. InP was easily etched in proportion to the amount of CBr_4, and provided a smooth surface; Al-containing layers could not be etched. This technique was very effective for obtaining a good regrowth interface and reducing the concentration of impurities. When CBr_4 was introduced during the selective growth of AlGaInAs layers, there were no polycrystals on the dielectric masks. Because CBr_4 did not adversely influence optical properties, this method is effective for fabricating compound semiconductor devices.

1. INTRODUCTION

Recently, demands to improve semiconductor optical devices for optical communication systems have been increasing. To realize devices with such high performance as uncooled operation and high-speed modulation, new materials and integration technique have been applied.

AlGaInAs/InP and GaInNAs/GaAs have advantages over conventional GaInAsP/InP lasers in terms of high-temperature operation. Integrated devices such as EA modulator integrated DFB-LD and wavelength-selectable LDs, which has an LD-array, an optical amplifier, and a passive waveguide, have been developed. Metalorganic chemical vapor deposition (MOCVD), which is the key technology for epitaxial growth, also needs to be improved to fabricate high-performance devices. In this paper, we report on new MOCVD techniques for developing AlGaInAs systems.

AlGaInAs includes aluminum, which has high reactivity. Aluminum reacts strongly with oxygen in air, and the surface of AlGaInAs is easily oxidized, so many defects are generated at the interface grown on the oxidized AlGaInAs layer. Aluminum also reacts with dielectric masks such as SiN and induces polycrystals on the mask during selective growth. To avoid these problems, an etching gas was introduced into the MOCVD reactor. It has been reported that this technique improves selectivity during selective growth 1)~3), *in-situ* etching in the reactor 4)~7), and surface cleaning 8). Materials containing chlorine, such as hydrogen chloride (HCl), arsenic trichloride ($AsCl_3$), and carbon chloride compounds ($C_xH_yCl_z$), are used as etching gases. The etching mechanism is such that the chlorine radical, which is thermally decomposed from Cl-containing gas in the high-temperature reactor, reacts with group-III atoms and forms a III-Cl compound. This compound is so volatile that it desorbs from the surface to the gas phase, and the remaining group-V atom, phosphorus or arsenic are also thermally removed from the surface.

Occasionally, these chloride materials damage the equipment and the environment as a result of their strong reactivity. In contrast, materials containing bromine have the advantage of lower corrosion than chlorine-containing materials. Among them, carbon tetrabromide (CBr_4) is widely used as a precursor for carbon doping in GaAs systems 9), 10), therefore, a high-quality material is commercially available.

For this paper, CBr_4 was used as the etching gas in MOCVD reactor for the first time. High-quality epitaxial growth on AlInAs layer using *in-situ* etching and high selectivity of the selective growth of AlGaInAs multiple quantum wells (MQW) were realized 11), 12).

2. EXPERIMENTAL METHOD

All experiments were executed in a low-pressure MOCVD reactor. CBr_4 was introduced into the reactor with hydrogen carrier gas. The concentration and the maximum flow rate were 0.08 % and 6.4 μmol/min, respectively. The temperature of the substrate was varied from 540 to 660°C.

SiN patterned masks were used for *in-situ* etching and selective growth. Scanning electron microscopy (SEM), secondary ion mass spectroscopy (SIMS), and photoluminescence (PL) were applied to the samples for estimating surface morphology, film thickness, contents, and optical properties. Broad contact-type LDs were fabricated to estimate laser characteristics.

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3. RESULTS AND DISCUSSION

3.1 *In-situ* Etching with CBr_4

3.1.1 Etching of InP

The InP wafer was etched in the MOCVD reactor with CBr_4 under PH_3 pressure. The surface after *in-situ* etching was very smooth and there were no surface defects. The etching rate of InP was proportional to the CBr_4 flow rate, as shown in Figure 1. The substrate temperature in the range from 540 to 660°C, and the PH_3 flow rate between 250 and 500 cc/min did not affect the etching rate.

Figure 2 shows the depth profile around the mask after etching. The etching rate near the mask edge was enhanced in comparison to the area that had no influence from the mask. This phenomenon was similar to enhancing the rate of selective growth, which was caused by lateral diffusion and migration of group-III sources supplied onto the mask. It was assumed that CBr_4 or Br radicals, which were supplied to the mask, contributed to increasing the etching rate around the mask edge.

The epitaxial growth of MOCVD is limited by the amount of group-III under normal conditions, in which the growth rate is independent of the growth temperature and the flow rate of the group-V sources. Etching InP with CBr_4 under the above conditions was also restricted by the amount of CBr_4, and it was assumed that the following etching process proceeds smoothly. Bromine radicals thermally decomposed from CBr_4 reacted with InP, and volatile In-Br compounds were formed. The compounds desorbed from the surface of the sample to the vapor phase, and the remaining P atoms were successively removed from the surface.

3.1.2 Etching the DH Structure

The GaInAsP and AlGaInAs DH structures with SiN stripe masks, as shown in Figure 3, were etched with CBr4. The thickness of the p-InP upper cladding layer was 300 nm. The substrate temperature and the flow rate of CBr_4 were 600°C and 3.2 μmol/min, respectively. The etching time was 30 minutes, which was sufficient to etch the upper cladding layer, and thus the GaInAsP or AlGaInAs layer was exposed to the gas containing CBr_4 for about 8 minutes.

Figure 4 shows SEM images of the samples after etching. In the GaInAsP sample (a), many residues remained on the surface, and the etching rate of the GaInAsP layer was very low. The limitation of this etching process under this condition was dominated by the desorption of As atoms from the surface, rather than removal of Ga-Br compounds[9].

For the AlGaInAs sample (b), a mirror-like surface was obtained and undercut etching of the upper cladding layer was observed after etching with CBr_4. It was assumed that Al-Br compounds could not desorb form the surface to the vapor phase under this condition, so etching was stopped at the top of the AlGaInAs layer. As a result, CBr_4 supplied onto the AlGaInAs surface laterally migrated and caused the undercut etching.

It was concluded that the etching effect of bromine was In»Ga>Al. This process was similar to the reverse reactions of halogen transport VPE, and its equilibrium con-

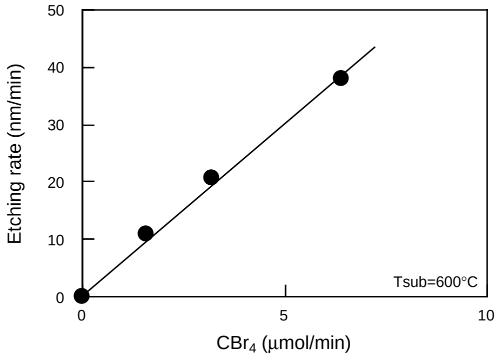

Figure 1 Dependence of etching rate on CBr_4 flow rate.

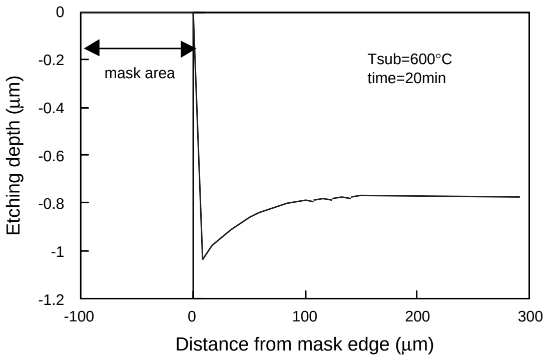

Figure 2 Depth profile of etched sample around mask.

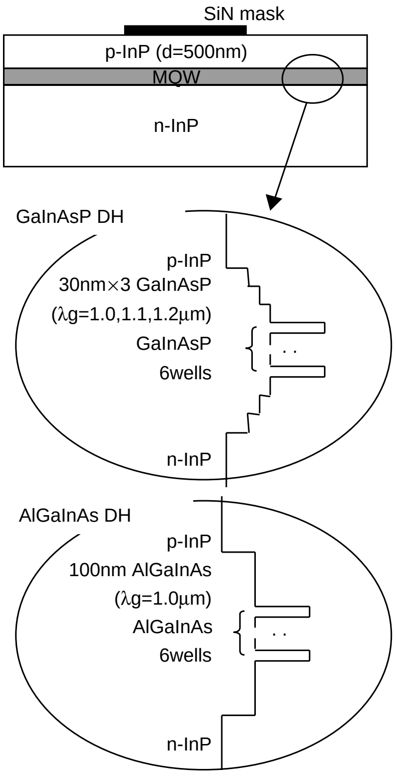

Figure 3 Structures of DH samples.

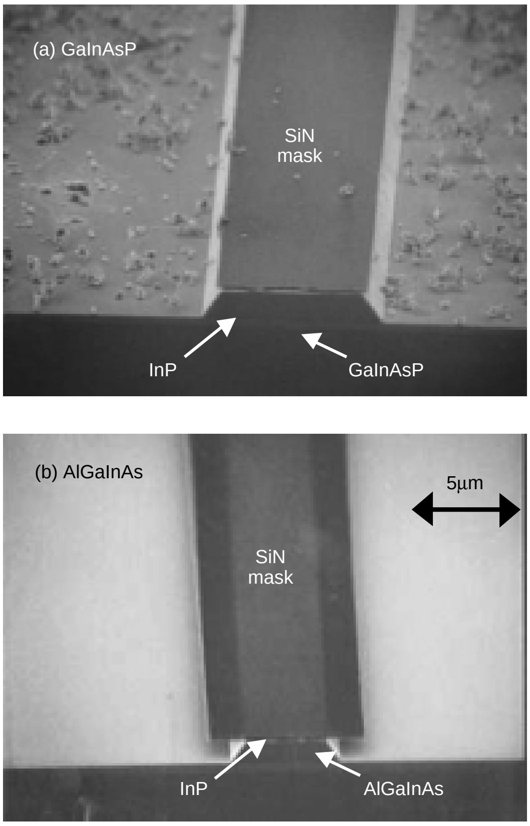

Figure 4 SEM pictures of samples after etching.

stants were InP<InAs<GaAs«AlAs 13), which was opposite tendency of the etching result.

3.1.3 Regrowth on *In-situ* Etched Sample

To confirm the advantages of *in-situ* etching with CBr$_4$, an AlInAs layer was successively grown on the AlGaInAs DH sample in the MOCVD reactor. We prepared the *ex-situ* sample, which was exposed to air before regrowth on the Al-containing layer for the reference.

SEM images after regrowth are shown in Figure 5. The smooth surface and high-quality crystal were obtained with the *in-situ* etching sample. On the contrary, the surface of the *ex-situ* sample was very rough and defects were observed at the interface of regrowth. The Al-containing layer was readily oxidized in air and caused degradation of the regrowth interface and the epitaxial layer. These results showed that *in-situ* etching was effective for improving regrowth on the Al-containing layer.

SIMS measurements were executed to estimate the impurities at the regrowth interface. An AlInAs layer was grown on an InP wafer with and without *in-situ* etching with CBr$_4$ for these measurements. The flow rate of CBr$_4$ and the etching time were 3.2 μmol/min and 3 minutes, respectively. The etching depth was 30 nm under this condition. The surface of the sample without etching was cleaned with sulfuric acid before growth.

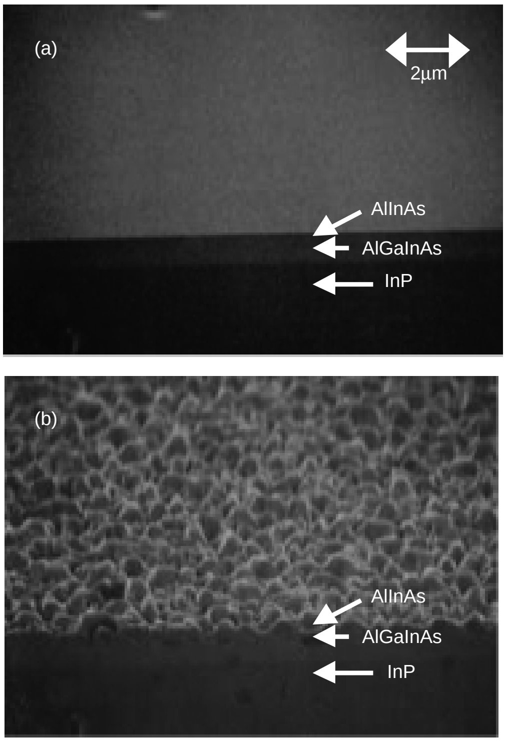

Figure 5 SEM pictures of samples after regrowth.

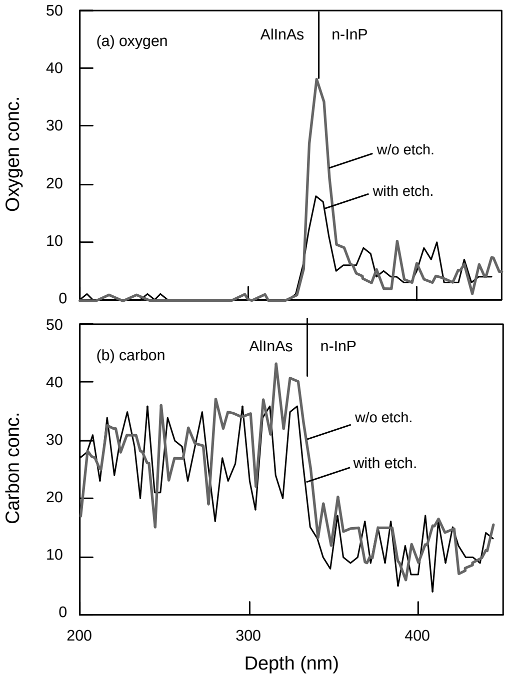

Figure 6 SIMS profile of impurities around regrowth interface.

The depth profiles of oxygen and carbon are shown in Figure 6. The solid and dotted lines indicate samples with and without *in-situ* etching, respectively. The oxygen concentration of the *in-situ* sample at the interface was markedly reduced, although both carbon profiles were almost the same. The oxygen adsorbed on the surface before growth was effectively removed by *in-situ* etching. Although carbon elimination at the interface was not clear, contamination of carbon on the surface during etching with CBr$_4$, which was the carbon dapant, was negligible. It was concluded that *in-situ* etching with CBr$_4$ had the advantage of a high-quality regrowth interface.

3.1.4 Improvement of *In-situ* Etching Characteristics

It was found that a rough surface was obtained after etching GaInAsP. It was also difficult to clean the oxidized surface of the Al-containing layer using CBr_4. It was assumed that these factors were partly due to the different etching rates of group-III. To improve the effects of surface cleaning, TMIn, which was the source material of indium, was introduced into the reactor during CBr_4 etching, because indium was the easiest specie to etch.

After *in-situ* etching with CBr_4, the MQW structure was grown on the AlInAs layer, whose surface was oxidized in air. The PL of the MQW was measured to estimate the quality of the growth interface. The flow rates of TMIn and CBr_4 were 3.8 μmol/min and 1.6 μmol/min, respectively. For the reference sample, *in-situ* etching was carried out without TMIn. The flow rate of CBr_4 for the reference sample was 0.3 μmol/min.

Figure 7 shows the etching time dependence of the PL intensity of the MQW, which was normalized by the MQW on the InP layer. There was no PL intensity without etching because of the surface oxidization. In the sample without TMIn, PL intensity was about 25 % at 10 sec etching, and decreased sharply with etching time. On the contrary, the maximum intensity of the sample with TMIn was about 75 %. The quality of epitaxial layers improved with the introduction of TMIn during *in-situ* etching. We confirmed the possibility of improving growth by supplying the source.

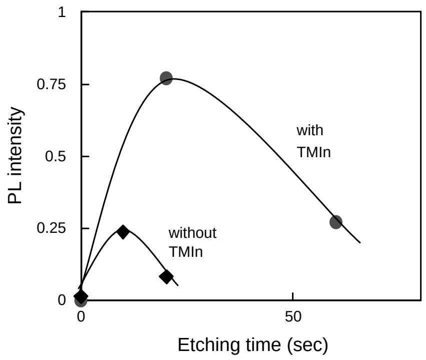

Figure 7 PL intensity of MQW grown on *in-situ* etched sample.

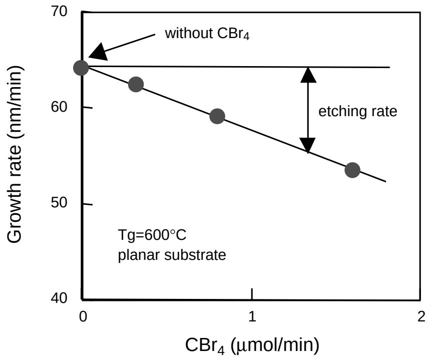

Figure 8 Dependence of growth rate of InP on CBr_4 flow rate.

3.2 Selective Growth of AlGaInAs with CBr_4

3.2.1 Introduction of CBr_4 during Growth

The etching effect of CBr_4 on InP and AlGaInAs during MOCVD growth was investigated. The relation between the flow rate of CBr_4 and the growth rate of InP is shown in Figure 8. Introducing CBr_4 during growth suppressed the growth rate, and the difference from that without CBr_4 was the etching effect. This etching rate was proportional to the amount of CBr_4, and it was the same as the etching rate in Figure 1. This relation did not depend on the growth rate and the flow rate of TMIn. It was assumed that the source of group-III supplied onto the sample partially reacted with bromide radicals, and was desorbed from the surface.

Figure 9 shows the results of the ternary compounds, AlInAs. The etching rate was proportional to the flow rate of CBr_4, and it was almost the same as that of InP. The aluminum content in AlInAs increased with the flow rate of CBr_4, and it was found that CBr_4 only etched indium. In the case of GaInAs, the results were the same as with AlInAs. It was concluded that indium was only etched with CBr_4 during growth for compounds including indium.

3.2.2 Selective Growth of AlGaInAs

Selective growth of AlGaInAs was examined. The patterned masks, which had an 80 μm width separated by a 20 μm opening, as shown in Figure 10, were used for selective growth. The growth structure was AlGaInAs DH, as shown in Figure 4. The flow rates of group-III sources were adjusted in consideration of the above results.

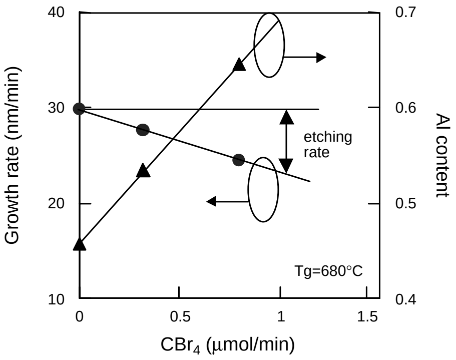

Figure 9 Dependence of growth rate and Al content of AlInAs on CBr_4 flow rate.

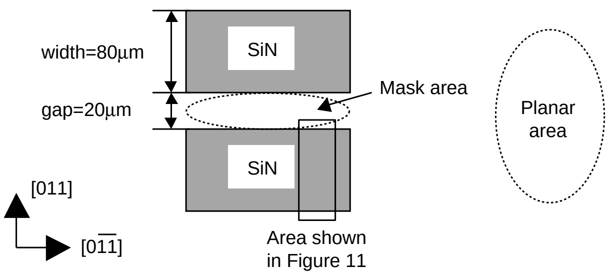

Figure 10 Mask pattern for selective growth.

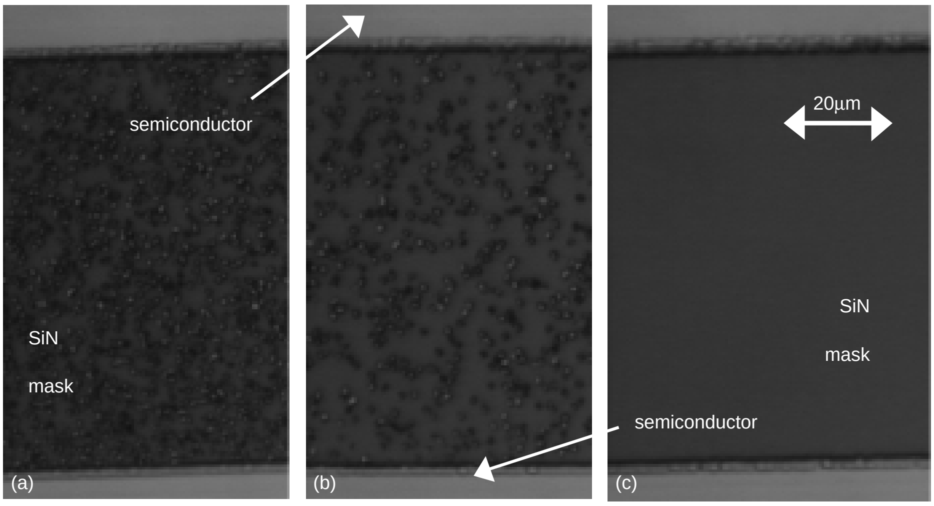

Figure 11 **Top views around mask area of as-grown sample.**

Many polycrystals remained on the mask without CBr_4 being supplied, as shown in Figure 11 (a). They decrease sharply with an increase of CBr_4, and no polycrystals are observed on the sample of CBr_4=3.2 µmol/min. An improvement of the selective growth of Al-containing materials was reported with a change of growth conditions [14),15)], such as low growth rate and low growth temperature. Our etching technique had an advantage for selective growth because the growth condition did not need to be changed from the optimized condition for AlGaInAs.

Growth enhancement at the mask edge was caused by the migration of group-III sources on the mask, and it was found that CBr_4 did not affect the extent of enhancement. CBr_4 did not etch the migration species on the mask but did etch the adsorbed atoms on the mask surface. The adsorbed atoms acted as the nuclei of polycrystals, so removing of the adsorbed atoms was very effective for decreasing the polycrystals. Although aluminum atoms in the AlInAs layer were not etched, the adsorbed aluminum atoms on the mask were easily removed. It was assumed that effective etching of aluminum on the mask was caused by the smaller amount of group-III species on the mask and the weaker bonding strength between Al and the mask.

3.2.3 Influence of CBr_4 on Optical Properties

The influence of CBr_4 on the optical properties of AlGaInAs QW was evaluated using PL and broad contact LDs of the planar area. The emission wavelength of all samples was set at 1300 nm. The dependence of characteristics on CBr_4 flow rate is shown in Figure 12. Although PL intensity became a little weaker as the CBr_4 flow rate increased, the threshold current density of LD was reduced. It was experimentally concluded that introducing CBr_4 during growth did not affect optical properties under this condition.

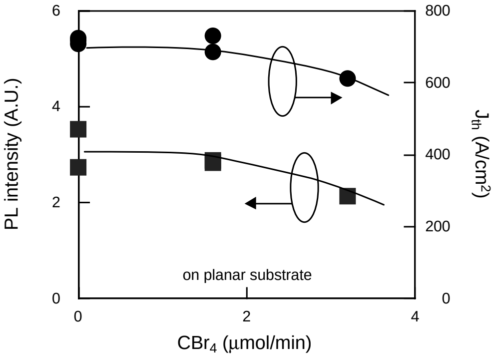

Figure 12 **Dependence of PL intensity and threshold current density on CBr_4 flow rate.**

4. CONCLUSION

In-situ etching of a compound semiconductor and selective epitaxial growth of an Al-containing material were realized in a metalorganic chemical vapor deposition (MOCVD) reactor using carbon tetrabromide (CBr_4). *In-situ* etching depended on the content of the compound semiconductor. InP was easily etched in proportion to the amount of CBr_4, and provided a smooth surface, and Al-containing layers could not be etched. This technique was very effective for obtaining a good regrowth interface and reducing the concentration of impurities. When CBr_4 was introduced during selective growth of AlGaInAs layers, there were no polycrystals on the dielectric masks. Because CBr_4 did not adversely influence optical properties, this technique is effective for fabricating devices.

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