Backside SIMS analysis of zinc profiles in InGaAsP

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We improved the depth resolution in a SIMS analysis of a zinc diffusion front in an InGaAsP laser diode by using a backside SIMS analysis. The optimum etching conditions were examined to remove the InP substrate and to acquire an InGaAsP mirror surface. We found that a $HCl:H_3PO_4$ solution of 2:3 had sufficient selectivity and that it reduced roughening on the InGaAsP surface. Using this solution, we controlled the roughening of the InGaAsP surface within 1nm. We used the backside SIMS to analyze the zinc profile and found that the steepness of the zinc profile decreased by almost half as much as the steepness of the zinc profile measured by the conventional SIMS (measuring from the surface). Using the depth resolution function, we found that the effects of atomic mixing and redeposition for both kinds of SIMS measurements are similar. We concluded that the steepness of the zinc profile measured by the backside SIMS depends on the leading side of the depth resolution function and that the steepness of the zinc profile measured by the conventional SIMS depends on the trailing side of the depth resolution function.

1. Introduction

Because zinc diffusing into active layers degrades the characteristics of an InGaAsP laser diode (LD), it is necessary to analyze the zinc diffusion front with a high-depth resolution. The diffusion front is the zinc distribution in an InGaAsP layer next to an InP layer doped with about 1×10^{18} atoms/cm^3 of zinc. A secondary ion mass spectrometry (SIMS) analysis of the zinc diffusion front is difficult due to ion-sputtering induced effects, such as surface roughening and atomic mixing. When an argon or oxygen primary ion beam is used, the InP layer is roughened even in low-energy sputtering and the depth resolution is degraded [1]. The roughening of the InP layer caused by a cesium primary ion beam was examined only in 17 keV, so the roughening in less than 10 keV remains unclear. Though cooling a sample at below −100 ℃ reduces the surface roughening of an InP layer, a detection limit, which is determined by the background noise level in a zinc profile, increases by more than one order due to water sticking on the sample. To avoid degradation in the depth resolution induced by ion sputtering, we used a backside SIMS analysis that has been used to examine contact metal diffusion in GaAs field effect transistors [2,3]. The backside SIMS analysis is a depth-profiling method using ion-sputtering from the backside after the removal of a sample substrate with a preferential chemical etching. In the SIMS analysis of a high-to-low concentrated region, atomic mixing and redeposition of sputtered atoms on the sample induces the tailing of an element profile. The backside SIMS analysis, which is measured from a low concentrated region to a high concentrated region, suppresses this tailing. In the backside SIMS analysis of the InGaAsP LD sample, it is expected that the removal of the InP substrate prevents roughening that might be induced by ion- sputtering.

In the InGaAsP LD system, etching conditions need to be optimized to remove the InP substrate and to acquire an InGaAsP mirror surface. In particular, the flatness of the InGaAsP surface must be carefully controlled in order to keep the depth resolution. In this work, we optimized the etching conditions and improved the depth resolution of the backside SIMS. Using the depth resolution function (DRF) [4,5], we will describe the improvement in the depth resolution.

2. Experimental

The InGaAsP LD samples grown on an InP substrate by metal organic vapor phase epitaxy (MOVPE) consisted of an InP layer (700 nm) and InGaAsP active layers (250 nm). Only the InP surface layer was doped with 3×

10^{17}-1 × 10^{18} atoms/cm^3 of zinc. We also prepared InGaAsP samples with arsenic compositions ranging from 0.22 to 0.87 in order to examine the dependence of arsenic secondary ion intensity on arsenic composition.

The SIMS analyses were done by using a CAMECA IMS-3f equipped with a magnetic sector mass analyzer. Using the 5.5-keV Cs^+ primary ion beam, we detected the CsM^+ cluster ions, where M means an element we analyzed. The CsM^+ is known to reduce the change of an ionization probability with a matrix composition (the matrix effect). A $CsAs^+$ profile was measured to judge the position of each layer. The crater depth was measured by using the stylus surface profilometer (DEKTAK 3ST) after SIMS measurements in order to convert a measuring time to the sputtered depth.

A mixed solution of HCl (36%) and H_3PO_4 (85%) was used at room temperature to remove the InP substrate. This solution selectively removed the InP rather than the InGaAsP. The etching stopped at the interface between the InGaAsP and the InP substrate. We optimized the ratio of the etching solution in order to acquire an InGaAsP mirror surface. Before etching, we stuck the InGaAsP LD sample upside-down on a silicon wafer with an epoxy resin and we mechanically polished the InP substrate to suppress etching damage. The remaining thickness of the sample was measured by using the stylus thickness monitor and the surface roughening was examined by using the stylus surface profilometer.

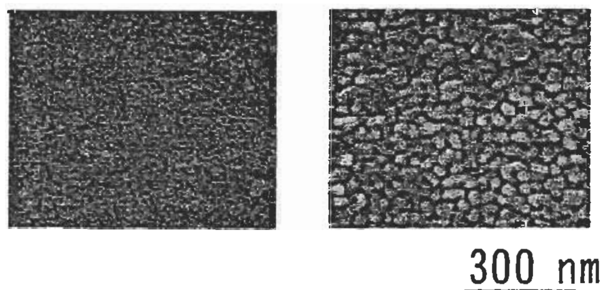

Figure 1. SEM images of the InGaAsP surfaces after preferential etching with the mixed solution of HCl and H_3PO_4. The ratios of the solution were HCl:H_3PO_4=2:3 (left) and 1:1 (right) .

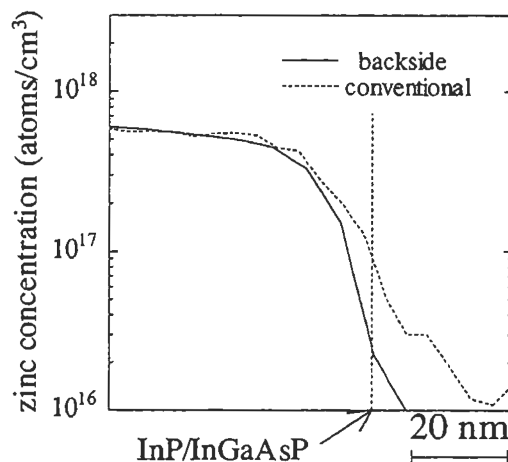

Figure 2. Zinc profiles measured by the conventional SIMS and the backside SIMS near the interface between the surface InP and the InGaAsP active layers.

3. Results and Discussion

We examined the optimum ratio of the HCl-H_3PO_4 solution for the InGaAsP mirror surface. We found that the etching rate increased as the HCl ratio became higher. But the solution, which more than half of its content was HCl, induced the InGaAsP surface roughening. Figure 1 shows the SEM images of the InGaAsP surface after etching. The HCl:H_3PO_4 solution of 2:3 reduced the surface roughening less than the 1:1 solution. For the 2:3 solution, the mean deviation of roughness was 0.8 nm and for the 1:1 solution, it was 2.4 nm. We used the 2:3 solution for the following backside SIMS analyses.

Figure 2 shows the zinc profiles by the conventional (measuring from the surface) SIMS and by the backside SIMS near the interface between the surface InP and the InGaAsP active layers. The steepness of the zinc profile measured by the backside SIMS was 13 nm/decade. This steepness was almost half as much as the steepness of the zinc profile measured by the conventional SIMS (20 nm/decade). Although zinc atoms seemed to diffuse into the active layers at nearly 1×10^{17} atoms/cm^3 in the conventional SIMS, much smaller amounts of zinc atoms were observed in the backside SIMS. Figure 3 shows the zinc profiles measured by the backside SIMS of the other samples with various doping

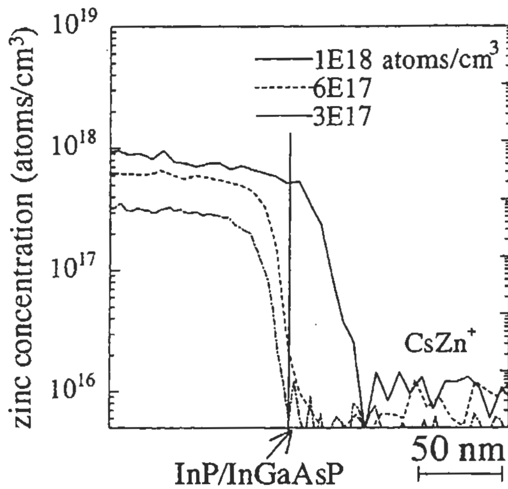

Figure 3. Zinc profiles measured by the backside SIMS analysis of the InGaAsP LD samples with various doping concentrations of zinc.

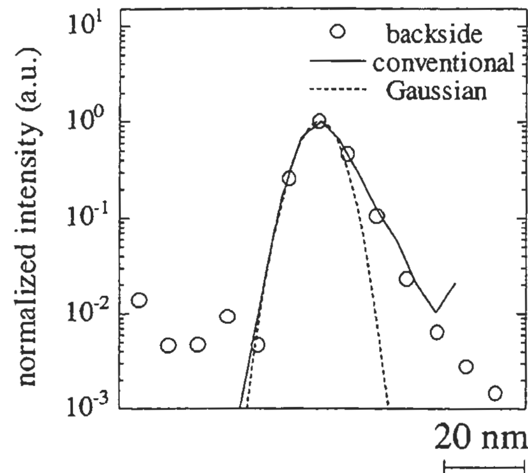

Figure 5. DRFs (normalized to unity) of the backside SIMS and the conventional SIMS. The broken line indicates the effect of surface roughening.

concentrations of zinc. When the zinc concentration is beyond 1×10^{18} atoms/cm^3, the zinc anomalously diffuses into the active layers. We found that when the zinc doping concentration is below 1×10^{18} atoms/cm^3, the degradation in the InGaAsP LD characteristics can be avoided.

We used the DRF of arsenic to investigate the improvement in the depth resolution by the backside SIMS. The DRF consists of a Gaussian function on the leading side and a Lorentzian one on the trailing side. In the MRI model, the Gaussian function represents the effect of surface roughening and the Lorentzian function represents the effect of atomic mixing [6]. To obtain the DRF, we examined the linearity of the $CsAs^+$ intensity versus the arsenic composition. Figure 4 shows the relationship between the $CsAs^+$ intensity in the InGaAsP and the arsenic composition. The $CsAs^+$ intensity was normalized by the CsP^+ intensity in the InP. The $CsAs^+$ intensity increases proportionally to the arsenic composition. This indicates that the matrix effect was suppressed by detecting the Cs cluster ions.

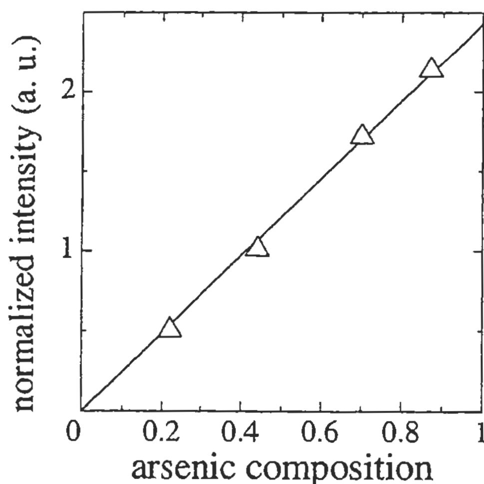

Figure 4. Relationship between the arsenic composition ratio and the $CsAs^+$ intensity in the InGaAsP layer. The $CsAs^+$ intensity was normalized by the CsP^+ intensity in the InP layer.

Figure 5 shows the DRFs (normalized to unity) for both of the SIMS methods. The DRFs were derived by differentiating step-function-like arsenic profiles in the InP/InGaAsP interfacial region. In the conventional SIMS, the surface roughening of the InP layer is likely to influence the shape of the DRF. The DRF becomes a Gaussian-like shape when there is a lot of surface roughening [7]. Sample cooling is known to reduce surface roughening of the InP layer. We found that there was no real difference between the DRF in the SIMS analysis at room temperature (RT) and at temperatures below −100℃. As shown in Fig. 5, the DRF at RT keeps an asymmetric shape in which the left half is given by the Gaussian function and in which the right half is given by the Lorentzian function. These results show that the effect of roughening the

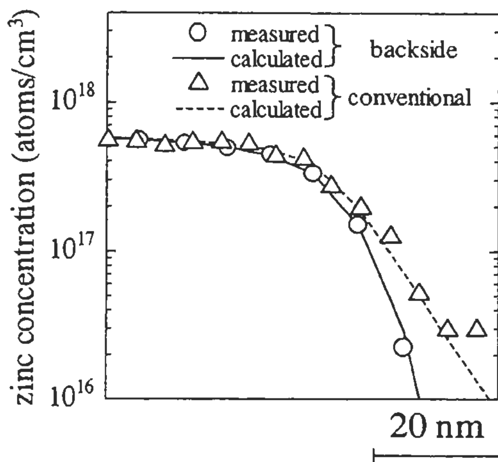

Figure 6. Convoluted and measured zinc profiles in the sample doped with 6×10^{17}-atoms/cm^3 zinc.

InP layer is negligible in distinguishing shapes of both sides of the DRF. In Fig. 5, the DRFs of the two SIMS methods are well in accordance. This suggests that the effects of the amount of atoms redeposited on the sample and the effects of atomic mixing are almost unchanged in both kinds of SIMS measurements of high-to-low and low-to-high concentrations of arsenic.

A measured SIMS profile can be given by convoluting an actual profile with the DRF. The observed steepness of the zinc diffusion front is affected by the leading side (Gaussian function) of the DRF in the backside SIMS and by the trailing side (Lorentzian function) of the DRF in the conventional SIMS. To determine the optimum model profile of the actual zinc distribution, we used the measured conventional-SIMS profile and the model DRF shown in Fig.5. We first convoluted model zinc profiles with the model DRF in the direction from the sample surface, and then fitted the convoluted profiles one by one with the measured conventional-SIMS profile. Finally, we obtained the optimum model zinc profile as the best-fitted result. The measured backside-SIMS result should be reconstructed by convoluting this obtained model zinc profile with the model DRF in the direction from the backside. Figure 6 shows the comparison between the convolution results and the measured zinc profiles of the $6\text{x}10^{17}$-atoms/cm^3 zinc-doping sample. The calculated backside-SIMS profile was well in accordance with the measured profile. It was concluded that the steepness of the backside SIMS mainly depends on the leading side of the DRF. In the backside SIMS analysis, the conditions for the preferential etching should be carefully controlled in order to obtain a high-depth resolution.

4. Conclusion

We investigated the zinc diffusion front in the InGaAsP LD by using the backside SIMS analysis. The optimum etching conditions were examined to remove the InP substrate completely and to acquire the InGaAsP mirror surface for the analysis. We found that the HCl:H_3PO_4 solution of 2:3 reduced the roughening on the InGaAsP surface. After removing the InP substrate by this solution, we used the backside SIMS to measure the zinc profiles in the InGaAsP active layers. As a result, the steepness of the zinc profile decreased compared to the conventional SIMS. Using the depth resolution function, we demonstrated that the steepness of the zinc profile measured by the backside SIMS mainly depends on the leading side of the depth resolution function.

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6. References

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