Quantitative Trace Analysis of Impurities in InP by SIMS

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This paper takes a detailed look at quantitative secondary ion mass spectrometry(SIMS) analysis has been performed to ascertain the electrically important impurities in InP. The SIMS analysis accuracy is estimated to ± 10 % by using standard InP crystals analyzed through chemical analysis. The SIMS detection limits are lowered to the $10^{12}-10^{15}$ cm^{-3} levels by careful detected ion choice. Analyses of four undoped crystals for liquid phase epitaxy use suggest that S is the major residual impurity.

1. INTRODUCTION

The quality of an undoped crystal must be closely examined when using InP single crystal for such InP-based devices as InGaAsP-InP lasers or InP FETs. Although Hall mobility and carrier concentration are useful means of assessing the electrically active impurity concentration, they provide no information into the exact chemical nature of the impurities.

In InP crystals, particular attention has been paid to residual impurities such as Fe, Ge, S, Se, Si, Sn and Te. Fe is the important impurity from an electrical characteristic viewpoint because of its ability to form a deep acceptor level in InP. The other elements are known to form shallow donor levels in InP.

As, Ga and Sb are isoelectronic impurities effective for reducing dislocation density in InP.[1] Accordingly, these impurities are also important enough to warrant control of their doping levels.

During the past decade the net carrier concentration of undoped InP single crystal has seen a steady reduction from 10^{17} to 10^{15} cm^{-3}.[2] To chemically analyze the impurities below the 10^{15} cm^{-3} level, a highly sensitive analysis method is essential. Even though mass spectrometry types such as secondary ion mass spectrometry (SIMS) and spark source mass spectrometry (SSMS) can successfully provide analytical data

from the 10^{15} cm^{-3} level, they can not yield quantitative data without employing standard samples.

In this work, we studied a highly sensitive and accurate method using SIMS for analyzing these ten impurity elements found in InP. The quantitation of SIMS was established using highly doped InP crystals as standard samples analyzed by inductively coupled plasma emission spectrometry (ICP). The SIMS analysis accuracy was carefully investigated and the detection limits were lowered in relation to the detected ion choice for each impurity.

2. EXPERIMENTAL

2.1 SAMPLE

All highly doped InP crystals were grown by the liquid encapsulated Czochralski (LEC) technique. As, Fe, Ga, Ge, S, Sb, Se, Si, Sn and Te were separately doped to more than 10^{18} cm^{-3} levels, except for the Fe-doped crystal whose level was 10^{16} cm^{-3}.

2.2 CHEMICAL ANALYSIS

Quantitative analyses were performed by ICP for highly doped crystals using an SPS-1100 spectrometer, except for the S-doped crystal. For As, Sb, Se and Sb, the hydride formation technique was used.

Furthermore, S analysis was carried out by colorimetry using the methylene blue method.

The typical quantitative analysis procedure employed is as follows. 0.1 g of InP crystal was dissolved with 2 ml of an acid mixture (HCl:HNO$_3$:H$_2$O=6:1:6), diluted with ultra-pure water to a 1 % solution, and then analyzed by ICP. For each impurity element, at least five standard solutions were prepared, which contained 1 % of InP and the known concentration of impurities for analysis.

2.3 SIMS ANALYSIS

SIMS analyses were performed using a CAMECA IMS-3F. 10.5 keV O$_2^+$ having a beam current of 1.5 μA was used as a primary ion during positive ion detection. 14.5 keV Cs$^+$ having a beam current of 0.2 μA was also utilized for detecting negative ions. The typical beam diameters were 70 μm in both cases. The primary ion beam was rastered to an area of 250 x 250 μm and the secondary ions emitted were detected from the 60-μm diameter area in the center of the rastered area.

3. RESULTS AND DISCUSSION

3.1 CHEMICAL ANALYSIS

ICP analysis accuracy is dependent on the ICP intensity variation (X_i) and chemical preparation reproductivity (X_c). The former was calculated from the standard deviation divided by the mean value of the intensities. The X_i values for all elements were found to be within ±10 %.

On the other hand, X_c was examined through repeated analyses. One analysis example, that of As, is given in Table 1. The standard and maximum deviations from the mean value were only 3.5 and 4.4 %. A reproductivity within ±5 % was verified in the analyses of the other impurity elements. It is clear from these results that the ICP accuracy successfully falls into ±10 % for all elements from these results.

Table 1. Analysis of As-doped InP.

Run	As result/cm^{-3}	Deviation/%
1	4.4 x 10^{20}	-2.2
2	4.5 x 10^{20}	0
3	4.7 x 10^{20}	+4.4
Mean value	4.5 x 10^{20}	

RSD was 3.5 % and maximum error was 4.4 %.

The impurity concentrations in highly doped crystals obtained by ICP analysis are summarized in Table 2 along with the SSMS results. Both results exhibited good agreement within the SSMS error, that is, c.a. ±30 %. These data also confirm that ICP analysis ensures good accuracy.

Table 2. The ICP impurity analysis of highly doped InP.

Element	ICP /cm^{-3}	SSMS /cm^{-3}
As	4.5 x 10^{20}	
Fe	5.5 x 10^{16}	9.4 x 10^{16}
Ga	2.7 x 10^{18}	3.7 x 10^{18}
Ge	2.9 x 10^{18}	
S[a]	9.3 x 10^{18}	
Sb	3.5 x 10^{18}	2.3 x 10^{18}
Se	1.6 x 10^{19}	
Si	2.1 x 10^{19}	
Sn	1.1 x 10^{18}	
Te	1.3 x 10^{18}	

a) This was the result from colorimetric analysis.

3.2 SIMS ANALYSIS

3.2.1 DETECTION LIMIT

In SIMS analysis, the instrument conditions often cause secondary ion intensity variation. To suppress this variation, we measured the intensity ratios of impurity atomic ions ($M^\pm$) to matrix ions (P^+, In^-). To obtain the lowest possible background level, molecular ions such as the oxide ions ($MO^\pm$) and compound ions having matrices ($MP^\pm$, $MIn^\pm$) were also detected as well as atomic ions ($M^\pm$).

The detection limit, d, is presented as

$$d = f \times r_b,$$

where f is the sensitivity factor and r_b is the background intensity ratio. The sensitivity factor f, was calculated from the intensity ratio divided by the impurity concentration obtained through ICP. A discussion will be given in the next section concerning the sensitivity factor. The background intensity ratio, r_b, of the objective elements was obtained by adopting the minimum intensity ratio measured for several undoped InP crystals.

The impurity element detection limits are summarized in Table 3, which were determined by putting both positive and negative ion results together. It is clear that Fe as a positive atomic ion has a lower detection limit than any other ion with an analysis level of 10^{14} cm^{-3} being realized.

Table 3. Sensitivity and detection limits for secondary ions of impurities in indium phosphide.

Element	ion	mass	sensitivity factor /cm^{-3}	background in-tensity ratio[a]	detection limit /cm^{-3}
As	AsP$^-$	- 106	1.4×10^{19}	2.2×10^{-4}	4×10^{15}
Fe	Fe$^+$	- 56	7.7×10^{19}	3.9×10^{-6} [b]	3×10^{14}
Ga	GaP$^-$	- 100	4.2×10^{18}	1.1×10^{-4}	5×10^{14}
Ge	GeP$^-$	- 101	1.3×10^{18}	4.6×10^{-5}	6×10^{13}
S	S$^-$	- 34	4.8×10^{18}	4.2×10^{-4}	2×10^{15}
Sb	SbP$^-$	- 152	1.4×10^{19}	2.1×10^{-5}	3×10^{14}
Se	Se$^-$	- 82	4.0×10^{18}	1.3×10^{-5}	5×10^{13}
Si	Si$^-$	- 28	7.9×10^{18}	1.1×10^{-5}	9×10^{13}
Sn	SnP$^-$	- 149	2.1×10^{18}	6.2×10^{-4}	1×10^{15}
Te	Te$^-$	- 130	7.7×10^{17}	8.6×10^{-5}	7×10^{12}

a) These ratios are the intensity ratios of impurity ions to ^{113}In$^-$.

b) This ratio is the intensity ratio of impurity ions to ^{31}P$^+$.

S, Se and Te were found to exhibit relatively low detection limits of their negative atomic ions (M$^-$). This corresponds to the ease in forming negative ions due to their high electro-negativities. Se and Te, which did not suffer contamination, exhibited extremely low detection limits of around 10^{12} cm^{-3}. This level seems to be the lower limit of the mass spectrometry detection system. Since the ^{32}S$^-$ intensity depended not merely on the contamination level present in the SIMS instrument but also on the spectrometrical interference of ^{32}O$_2$$^-$, detecting ^{34}S$^-$ instead of ^{32}S$^-$ achieved a detection limit of 2×10^{15} cm^{-3}.

While Si, Ge and Sn atomic ions do not have a high ion yield in positive or negative ions, compound ions of these elements having matrices have surprisingly high ion yields. Especially for the latter two, their detection limit can be lowered to 10-100 times over than their atomic ions using negative compound ions combined with P. Although this is thought to be due to the stability of the compound ions themselves, more extensive studies are necessary to confirm this interpretation.

Also for other elements, negative compound ions having P were found to exhibit lower detection limits than other ions. The positive atomic ion of Ga was indicated as being sensitive, but the lowest detection limit was actually obtained in the negative MP$^-$ ion because of its lower ion background ratio. The detection limits of the compound ions with P are comparable to that of the atomic ions in As and Sb analyses.

For all elements, detection limits of 10^{15} cm^{-3} were reached at the very worst, which are cosiderably lower values compared with those reported by Leta et al.[3]

3.2.3 ACCURACY

The accuracy can be influenced by reproductivity in terms of the sensitivity factor, f, and variation in secondary ion intensity. The variation originates from the variation in primary ion intensity and from the influence of sample morphology. Under optimum conditions, the variation falls at the very worst to ±5 %. The reproductivity is mainly dependent on the accuracy of chemical analysis (ca.±10 %). Consequently, the accuracy of SIMS analysis can be determined by the accuracy of chemical analysis, and can be estimated to be ±10 %.

3.3 APPLICATION TO UNDOPED CRYSTALS

Table 4 summarizes the analytical results of four undoped crystals for liquid phase epitaxy (LPE). S and Si are known to be the major residual donor impurities with their concentration levels thought to be 10^{16} cm^{-3}.[4] The Si values of the four samples were found to be close to the SIMS background level at 4×10^{14} cm^{-3}. This indicates that these crystals are free of Si contaminations during crystal growth. S was detected in all samples and the S concentrations were 7×10^{15} cm^{-3} on the average. Comparing the S levels obtained here with the carrier concentration

Table 4. SIMS analysis results of undoped InP (cm-3).

Element	1(s)	2(s)	3(p)	4(p)
As	4×10^{15}	4×10^{15}	4×10^{15}	4×10^{15}
Fe	3×10^{14}	3×10^{14}	3×10^{14}	3×10^{14}
Ga	5×10^{14}	5×10^{14}	5×10^{14}	5×10^{14}
Ge	6×10^{13}	6×10^{13}	6×10^{13}	6×10^{14}
S	7.3×10^{15}	5.2×10^{15}	9.8×10^{15}	4.6×10^{15}
Sb	3×10^{14}	3×10^{14}	3×10^{14}	3×10^{14}
Se	5×10^{13}	5×10^{13}	5×10^{13}	5×10^{13}
Si	9×10^{13}	9×10^{13}	9×10^{13}	9×10^{13}
Sn	1×10^{15}	1×10^{15}	1×10^{15}	1×10^{15}
Te	7×10^{12}	7×10^{12}	7×10^{12}	7×10^{13}

(m) and (p) indicate single crystal and polycrystal respectively.

levels of 3-7 x 10^{15} cm^{-3} in these undoped crystals, S seems to be the predominant impurity in the carrier.

The Fe values were also found to be below the background level (3 x 10^{14} cm^{-3}). As the Fe levels obtained here were much lower than the carrier concentration levels, Fe was found to only slightly contribute to the electrical characteristics. The obtained values of all other elements were below the SIMS background levels. Consequently, these elements are not introduced without intentional doping, that is, they are not subjected to contamination. These results suggest that InP crystals commonly used for LPE should be contaminated mainly by S.

4. CONCLUSION

SIMS quantitation was performed for impurities in InP through chemical analyses of ten elements. The study showed that the accuracy of the quantitative SIMS analysis is within ±10 %. Low detection limit levels of 10^{12}-10^{15} cm^{-3} were obtained by selecting particular ions such as compound ions consisting of the impurity and the matrix element. The analyses of four undoped InP crystals intended for LPE use suggested that S should be the major impurity in these undoped crystals.

REFERENCES

1)G.Jacob,M.Duseaux,J.P.Farges,M.M.B.van den Boom and P.J.Roksnoer, J.Crystal Growth,61,417(1983).
2)B.Cockayne,W.R.Macewan and G.T.Brown, J.Mater. Sci.,15,2785(1980).
3)D.P.Leta and G.H.Morrison, Anal.Chem.,52,514, (1983).
4)A.Yamamoto,S.Shinoyama and C.Uemura, J.Electrochem.Soc.,128,585(1981).