Instrumental Effects on Sensitivity Factors in Secondary Neutral Mass Spectrometry Measurements

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Some instrumental effects on sensitivity factors in SNMS (secondary or sputtered neutral mass spectrometer) have been investigated with III-V semiconductors, viz., GaAs, GaP and InP. There is a large variation of sensitivity factors, affected by target potential, ion optics setting and multiplier voltage, which is related to the mass difference between component elements. But relatively small variation of sensitivity factors by plasma conditions was found.

Keywords Secondary neutral mass spectrometry, relative sensitivity factor

SNMS (secondary, or sputtered neutral mass spectrometer) has received a lot of attention because of its advantages in quantification and depth resolution.¹⁻¹¹ Principle and instrumental reality of INA-3 are described elsewhere.^{1,3,4,10} Some instrumental effects of INA-3 (Leybold) on relative intensities, from which sensitivity factors can be calculated, have been investigated on III-V semiconductors. In order to discuss quantification of solid mass spectrometer, sputtering process and atomization, ionization process, ion transfer process, and detection process have to be examined. These processes are influenced by target potential, plasma condition, ion optics setting, and multiplier condition in the case of INA-3. The effects of ion optics of INA-3 have been investigated and are described in ref. 12. Briefly, intensity ratios change very much by ion optics setting condition, depending on mass difference between the constituents; in the case of GaAs the variation of intensity ratios was less than 20%, while for InP it was more than 200%.

In this report, the effects of target potential, plasma conditions and multiplier condition on sensitivity factors will be discussed. Since sputtering process and ionization process are separated, SNMS should be free of matrix effect compared with SIMS (Secondary Ion Mass Spectrometer). Although it has been said that comparatively uniform sensitivity factors can be obtained^{1,4}, strong variation of sensitivity factors with these instrumental parameters are found.

Experimental

III-V typed semiconductors, GaAs, GaP and InP, supplied by Showa Denko K.K., Tokyo were measured,

because of their simple compositions, and because the mass differences between the constituent elements cover a wide range from 6 (GaAs) to 84 (InP).

Figure 1 shows the scheme of INA-3 system, and the

Fig. 1 Scheme of INA-3 system.

Table 1 Basic experimental conditions

Target potential	-250 V
Plasma conditions	RF power 200 W, coil current 5.5 A, Ar gas pressure 3×10^{-3} mbar
Ion optics	tuned with InP wafer ¹²
Electron multiplier	multiplier voltage: 2.9 kV conversion voltage: -2.7 kV

location of each parameter to be discussed is indicated. Basic experimental conditions are shown in Table 1. While one condition was varied for investigation, the others were fixed to these values. Each intensity of ^{69}Ga , ^{75}As , ^{31}P , ^{115}In , was recorded and relative intensities (III/V) were calculated. The quadrupole mass spectrometer was tuned to the optimum peak resolution as well as sufficient sensitivity for the Pb isotopes using a Cu/Al alloy containing 0.08 wt% Pb.

Result and Discussion

Target potential

In SNMS measurement, a sample is biased to minus voltage to be sputtered with Ar^+ ions from the plasma. Target potential means this negative voltage to extract (or accelerate) the Ar^+ ions toward the sample surface. Intensity ratio depends strongly on target potential (Fig. 2): GaAs and InP give 60 and 200% variation of intensity ratios, respectively, between for the target potential -200 and -1000 V.

Wucher *et al.* found such target potential dependency with alloy measurements and attributed it to angular dependency.^{11,13} Their argument is that the emitted neutrals of different elements have different angular distributions and different dependency on target potential. But we can't subscribe to this argument; first, since sputtered particles are almost neutral it is thought that angular distributions of neutrals are not affected by the change of electric potential between the plasma and the sample. Second, our samples were single crystal semiconductor wafers; therefore, if such angular dependency occurred, the angular distributions of emitted particles should depend on the azimuthal angle of the sample plane. But in spite of setting direction, each wafer shows the same increasing tendency; especially in the case of InP, two measurements in different azimuthal angles gave almost identical tendency. In this SNMS instrument, primary Ar^+ ions come from all directions to sample plane and the entrance lens is normal to the sample plane (see Fig. 1), therefore it is thought that angular dependency should be canceled.

Fig. 2 Effect of target potential on intensity ratio.

It is well known that preferential sputtering can be found in III-V semiconductors even at low sputtering voltage¹⁴⁻¹⁶ and the degree of preferential sputtering in InP is larger than that of GaAs.¹⁶ We cannot give a precise interpretation here, but we suppose that preferential sputtering caused by low energy ion bombardment leads to target potential dependency.

Plasma conditions

The low-pressure Ar gas discharge is excited inductively by means of a excitation coil which is connected

Fig. 3 Effect of RF power on intensity ratio.

Fig. 4 Effect of coil current on intensity ratio.

Fig. 5 Effect of Ar gas pressure on intensity ratio.

to a 27.1 MHz RF generator. The effects of plasma conditions such as RF power, coil current and Ar gas pressure on intensity ratios were investigated. Intensity ratio depends on RF power and Ar pressure, but not on coil current (Figs. 3–5). Beyond the ranges of these parameters shown in these figures, the plasma could not be ignited. Although the intensity ratio depends on plasma conditions, the degrees of variations are relatively small, at most within 30% even in the case of InP. The degree of plasma condition dependency is larger in InP than that in GaAs.

Electron multiplier voltage

Intensity ratios vary largely with electron multiplier voltage (Fig. 6). The variation of the intensity ratios in InP is more than 200% between 2.8 and 3.3 kV. The effect is not caused by saturation effects of detector, because this voltage dependency can be found both in two cases, viz., target potential -250 V (absolute intensity *ca.* 3×10^4 cps at multiplier voltage 3.2 kV) and -1000 V (*ca.* 5×10^5 cps at 3.2 kV).

Our recent result of SIMS (Hitachi IMA-3), whose multiplier can be used both in direct counting (DC) mode and pulse counting (PC) mode, has revealed that the voltage dependency of intensity ratio was found only in PC mode. The present INA-3 system uses only PC mode. In this mode, ions of restricted energy collide on the first dynode and generate pulses which have a pulse height distribution (PHD). The collision and the energy transfer mechanism might be different between heavy elements and light ones, giving different PHD. Since the shape of the PHD is affected by the multiplier voltage, the intensity ratios will vary and show multiplier

Fig. 6 Effect of multiplier voltage on intensity ratio.

voltage dependency.

Effect of operating conditions

Effect of operating conditions on sensitivity factors is tabulated in Table 2, along with the effect of ion optics reported previously.¹² It can be easily found that the effects of plasma conditions are relatively small, while ion optics conditions, target potential and pulse counting voltage give very large variations on sensitivity factors, showing mass dependency.

Round-robin measurements were performed with Al alloy between INA-3 users in Germany;¹⁷ the sensitivity factors to Al, $D_{X,Al}$ (X is Si, Mg, Fe, Cu, etc.), were obtained. The results showed a large scatter of each $D_{X,Al}$ between the participants, and the degree of the scatter of $D_{X,Al}$ depended on mass difference between X and Al (see Fig. 7 in ref. 12). Figure 7 shows the relation between the maximum scatter $S_{X,Al}^{max}$ (calculated by division of the maximum value of sensitivity factor among the participants by the minimum value among them) and the mass difference between Al and each alloying element. Large variation of each $D_{X,Al}$ and the mass dependency of S^{max} can also be found. In these measurements, target potential was fixed to -1000 V, but

Fig. 7 Comparison of mass difference dependency of $S_{X,Al}^{max}$ (see text) obtained in round-robin measurements (closed circle) and calculated $S_{III/V}^{max}$ from Table 2 (open circle).

Table 2 Comparison of the degree of the intensity ratio variation

	ΔM	Target potential (-100 – -1000 V)	Plasma condition			Ion optics ¹² (90% range)	Multiplier voltage ^a
			RF power (200–280 W)	Coil current (5.5–4.8 A)	Ar gas ($3-4 \times 10^{-3}$ mbar)		
GaAs	6	1.45	1.04	1.01	1.03	1.15	1.13
GaP	38	2.91	1.15	1.03	1.20	1.80	2.42
InP	84	3.44	1.38	1.05	1.18	3.39	3.20

Condition ranges are shown in parentheses. a. 2.8–3.3 kV at target potential -500 V.

other conditions were on users choice. Because the effects of ion optics, plasma conditions and multiplier voltage are independent of each other, the maximum scatter, $S^{\max}$ for GaAs, GaP and InP can be estimated from Table 2, giving 1.4, 6.2, 18.5, respectively. These values are also plotted in Fig. 7. It can be said that the degree of the variations and mass dependency calculated from Table 2 are very similar to those of $S_{X,Al}$ obtained in round-robin measurement.

From our examinations, the large scatter $S_{X,Al}^{\max}$ of each $D_{X,Al}$ depending on mass difference to Al can be explained by the effects of plasma conditions, ion optic and multiplier voltage, mainly the latter two. The mass dependency of $S^{\max}$ can also be explained by the mass dependency of each effect.

In conclusion, the plasma condition causes variation of sensitivity factors, however, the variation is relatively small, at most within 30% in the case of InP. On the other hand, target potential, ion optics condition and multiplier voltage cause variations, more than 200% in the case of InP. The variation of intensity ratio of InP is much larger than that of GaAs in every case. This is thought to be due to mass difference effects.

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