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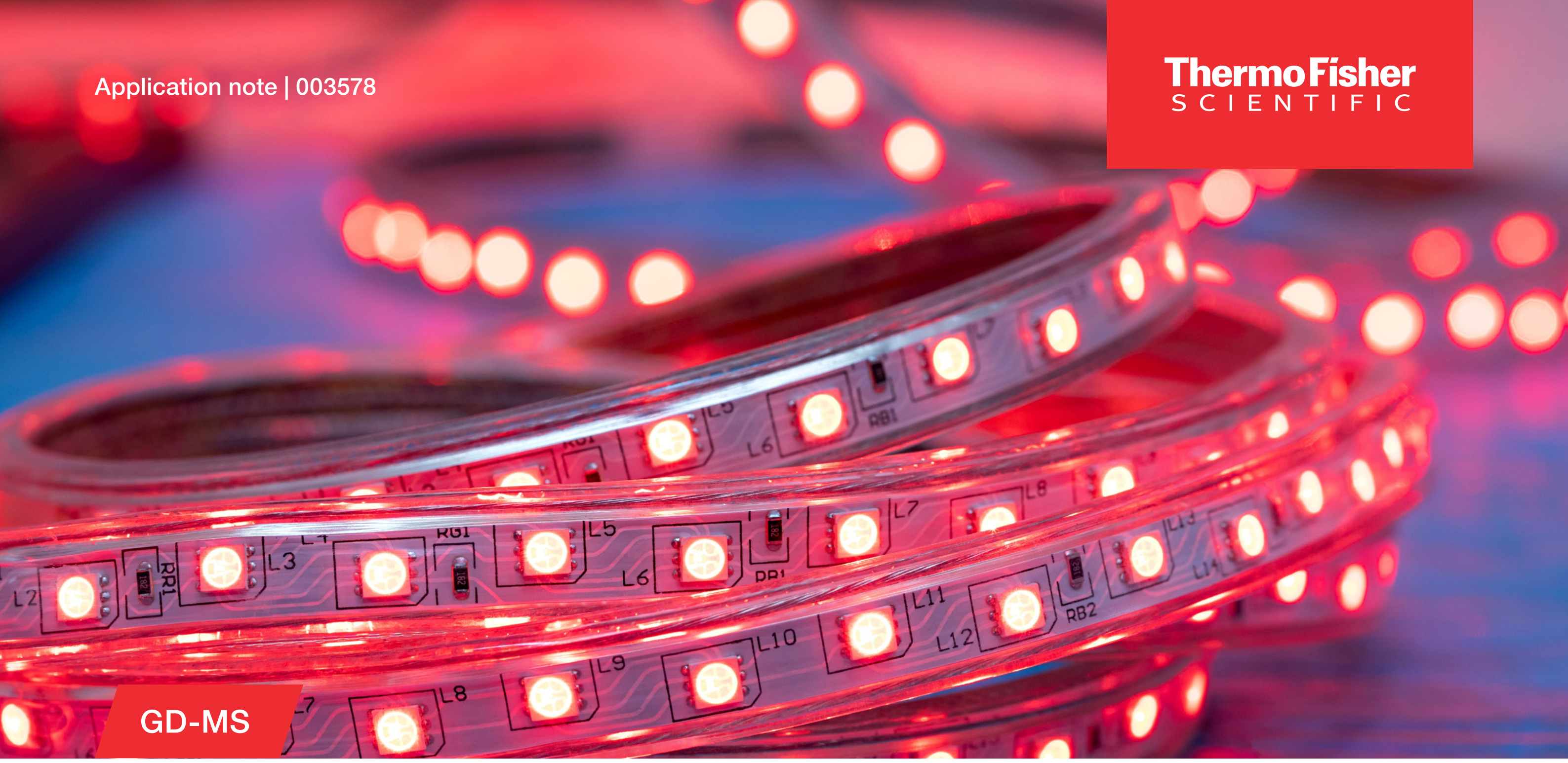

GD-MS

Routine analysis of 7N high purity gallium phosphide by Glow Discharge Mass Spectrometry

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Introduction

Gallium phosphide (GaP) is a semiconductor material used in electronic and optoelectronic devices, including light-emitting Diodes (LEDs), solar cells as well as high-frequency and high-power electronics[1-5]. GaP wafers offer several advances over traditional silicon wafers, including high efficiency, high-speed operation, and high-power handling capabilities[4-5].

This application note describes the direct analysis of impurities in high purity gallium phosphide with sub-ppb detection limits using the Thermo Scientific™ Element GD PLUS™ GD Mass Spectrometer.

Experiment

The flat samples are analyzed directly, with no digestion required. Instrumental conditions for the analysis with the Element GD PLUS GD-MS are shown in Table 1. Potential sample surface contaminations were removed by short presputtering within the instrument.

Method development

The developed method ensures a reliable separation of interferences from the analyte ions. The interferences PO, POH and GaGa could potentially lead to falsely high Ti, Ba and Ce results. The formation of these interferences is low in the fast-flow source of the Element GD PLUS GD-MS: $^{69}Ga^{69}Ga/^{69}Ga \approx 1$ ppm and $(^{31}P^{16}O^{1}H + {}^{31}P^{17}O)/^{31}P \approx 10$ ppm. They can easily be resolved at Medium Mass Resolution ($R = M / \Delta m = 4000$). This is visualized in the mass scans shown in Figures 1 and 2 with much wider mass windows than later being used for quantification. Therefore, the Medium Mass Resolution of the Element GD PLUS GD-MS enables interference free measurements of Ti, Ba and Ce in GaP matrix.

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Table 1: Element GD PLUS GD-MS instrument conditions for analyzing gallium phosphide

Discharge voltage	1000 V
Discharge current	≈ 17 mA
Mode	Pulsed DC
Pulse duration	90 µs
Pulse frequency	2 kHz
Discharge gas	500 mL/min Ar
Source pressure	1.05 mbar
Source temperature	15 °C
Anode parts	Graphite
Matrix sensitivity	1.5 x 10^{10} cps Ga + P in medium resolution, equivalent to ≈ 2.4 nA
Presputter time	5 min
Integration time	≈ 15 min for a measurement, consisting of 9 scans, for a suite of 70 elements
Sample throughput	≈ 2 - 3 samples per hour

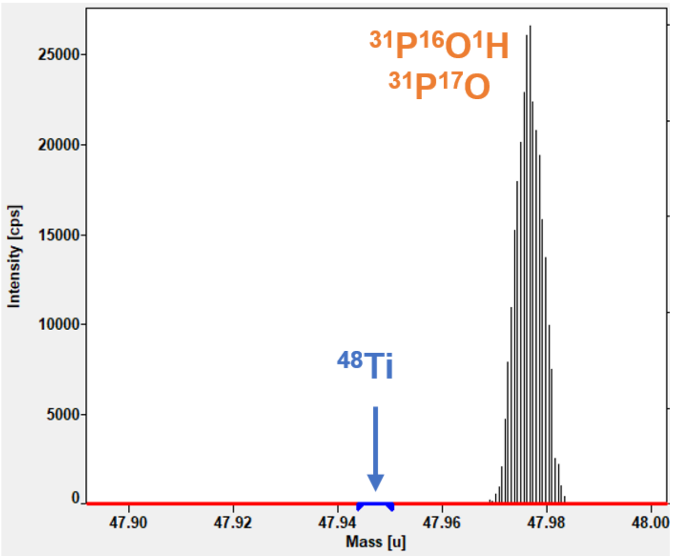

Figure 1: $^{31}P^{17}O$ and $^{31}P^{16}O^{1}H$ are fully resolved from ^{48}Ti in medium resolution (R=4000)

Silver is another example for an element that is prone to interferences. Both silver isotopes, ^{107}Ag and ^{109}Ag, could be interfered by GaAr interferences. The source design and mass resolution of the Element GD PLUS GD-MS eliminate these interferences by:

- The fast-flow GD source design, which reduces the formation of polyatomic interferences. The ratio $^{71}Ga^{36}Ar/(^{69}Ga+^{71}Ga)$ was only 1.6 ppm.
- High mass resolution (R=10000) that separates GaAr interferences from Ag efficiently. Figure 3 visualizes the interference spectrum in high resolution around the ^{107}Ag peak with a wide mass window to show the interferences. For routine measurements, a mass window size is used that contains only the ^{107}Ag mass.

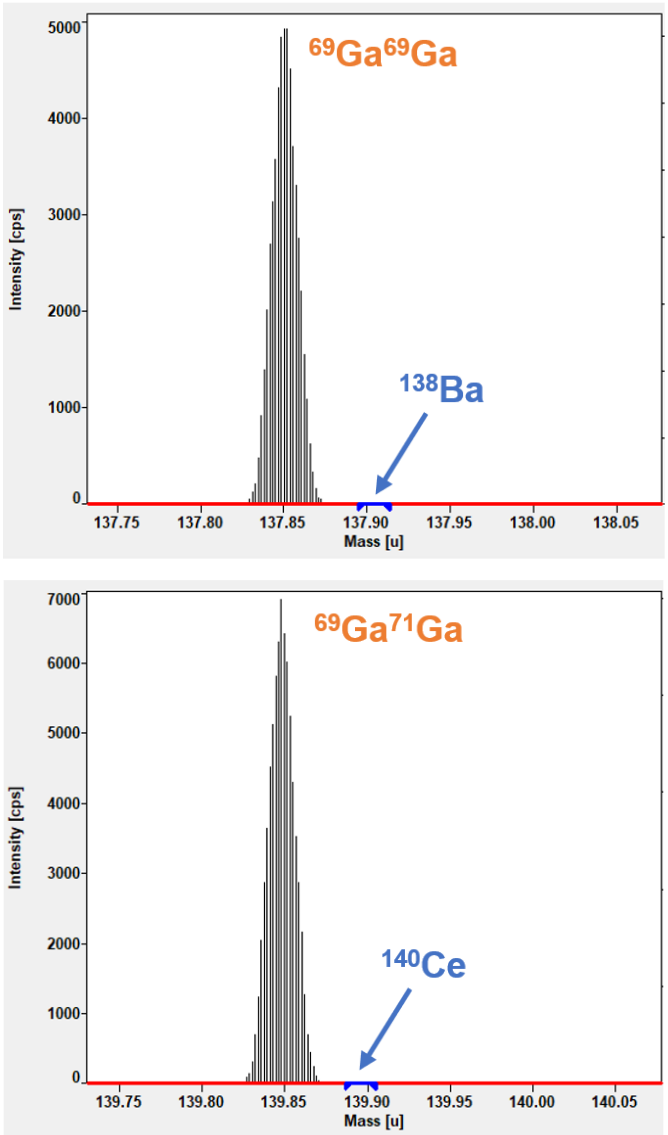

Figure 2: GaGa interferences are fully resolved from ^{138}Ba (top) and ^{140}Ce (bottom) in medium resolution (R=4000)

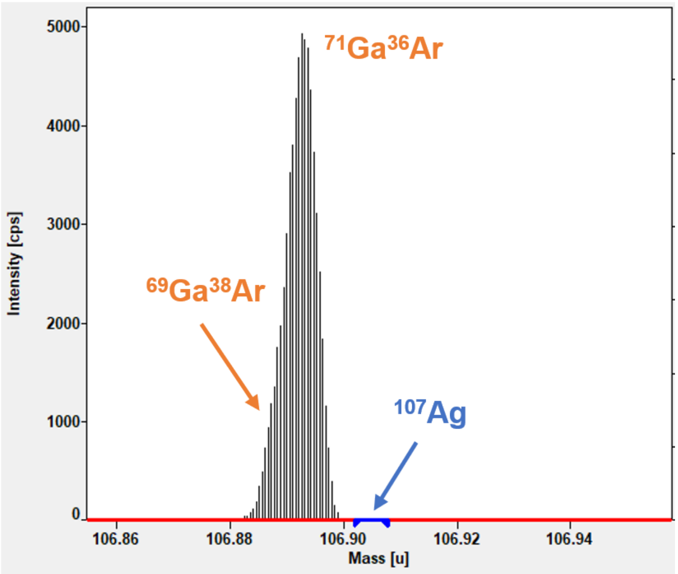

Figure 3: $^{71}Ga^{36}Ar$ and $^{69}Ga^{38}Ar$ are fully resolved from ^{107}Ag in high resolution (R=10000)

Because of the high sensitivity enabled by the fast-flow source design of the instrument, the Ag intensity in high resolution can be reliably quantified with a detection limit of 1 ppb.

Other examples for isotopes that benefit from the fast-flow GD source design are the isotopes of antimony because of the neglectable formation of triatomic interferences in this source; $^{71}Ga^{40}Ar^{12}C/(^{69}Ga+^{71}Ga) < 0.1$ ppb. This enables that antimony can be quantified with a detection limit of 0.5 ppb.

Germanium determination in gallium containing matrix could be negatively affected by abundance sensitivity, which is the tailing from a high matrix signal onto neighboring masses, that might lead to elevated background signals. The reverse Nier-Johnson geometry of the Element GD PLUS GD-MS leads to a reduced abundance sensitivity (71.92 u/^{71}Ga) in medium resolution of < 0.01 ppm, allowing germanium quantification at the < 1 ppb level.

Because of the low formation of polyatomic interference in the fast-flow source design, the reliable separation of interferences in medium or high mass resolution, the outstanding peak stability and the low abundance sensitivity, the data can be evaluated automatically, and no manual peak integration is required, making the routine analysis of ultraclean GaP straightforward and fast.

Results and discussion

Figure 4 shows the intensities of the Ga and P matrix signals. Because of the high efficiency of the fast-flow source design, a total matrix signal of 1.5 x 10^{10} cps (equaling 2.4 nA) is achieved, calculated as the sum of the ^{31}P and both Ga isotopes in medium resolution. Together with low background noise and reliable separation of interferences, this ensures low limits of detection to analyze ultraclean GaP.

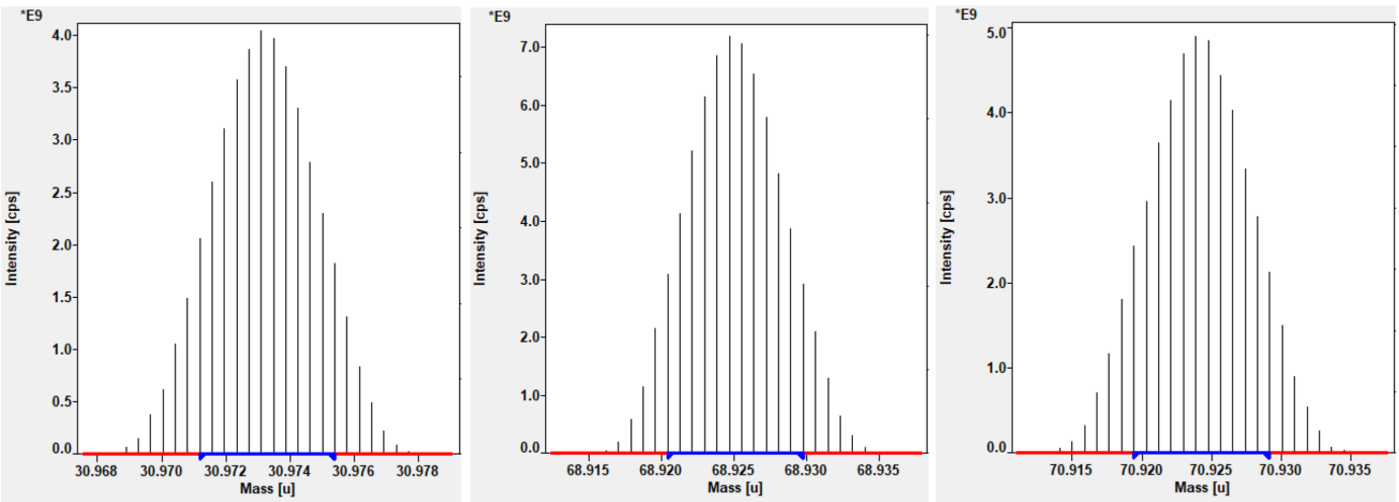

Figure 4: Matrix signals for ^{31}P, ^{69}Ga and ^{71}Ga of GaP analysis in medium resolution

Table 2 shows the mass fractions of a 7N GaP sample. These mass fractions were calculated from the ion beam ratios by the Element GD PLUS software using its standard Relative Sensitivity Factor (RSF) table. The RSF approach enables determining elemental concentrations rapidly within a single scan without the need for standard reference materials. This approach is common practice in GD-MS analysis, yielding in semiquantitative results that typically fall within 30 % of the true values. Due to the lack of certified gallium phosphide reference materials, all data shown here are therefore semiquantitative results. Additionally, the estimated limits of detections are shown in table 2. These values are calculated as three times the standard deviation of five consecutive analysis of a clean gallium phosphide sample.

The limits of detection are well below 1 ppb for most elements. The sum of all impurities in the gallium phosphide sample is below 50 ppb. Therefore, the GaP sample has a purity of 7N (>99.99999 %).

Table 2: Semiquantitative results and limits of detection for GaP analysis

Element	Mass	Mass fraction [ppb]	LoD [ppb]	Element	Mass	Mass fraction [ppb]	LoD [ppb]
Li	7	< LoD	0.05	In	115	< LoD	0.2
Be	9	< LoD	0.05	Sn	117	0.6	0.5
B	11	0.3	0.2	Sb	123	< LoD	0.5
Na	23	< LoD	0.5	Te	128	< LoD	0.5
Mg	24	< LoD	0.2	Cs	133	< LoD	0.05
Al	27	2.6	1	Ba	138	< LoD	0.05
Si	28	11	4	La	139	< LoD	0.05
S	32	11	3	Ce	140	< LoD	0.05
K	39	0.2	0.2	Pr	141	< LoD	0.05
Ca	44	0.6	0.3	Nd	142	< LoD	0.2
Sc	45	< LoD	0.05	Sm	152	< LoD	0.1
Ti	48	< LoD	0.05	Eu	153	< LoD	0.1
V	51	< LoD	0.05	Gd	158	< LoD	0.1
Cr	52	< LoD	0.1	Tb	159	< LoD	0.05
Mn	55	< LoD	0.1	Dy	164	< LoD	0.1
Fe	56	0.1	0.1	Ho	165	< LoD	0.05
Ni	58	< LoD	0.05	Er	166	< LoD	0.2
Co	59	< LoD	0.05	Tm	169	< LoD	0.1
Cu	63	< LoD	1	Yb	172	< LoD	0.1
Zn	64	< LoD	1	Lu	175	< LoD	0.05
Ge	73	0.7	0.2	Hf	178	< LoD	0.1
As	75	1.1	1	Ta	181	< LoD	5
Se	82	1.1	1	W	184	< LoD	0.1
Rb	85	< LoD	0.05	Re	187	< LoD	0.05
Sr	88	< LoD	0.05	Os	192	< LoD	0.2
Y	89	< LoD	0.05	Ir	193	< LoD	0.2
Zr	90	< LoD	0.1	Pt	195	< LoD	0.2
Nb	93	< LoD	0.05	Au	197	< LoD	0.2
Mo	98	< LoD	0.2	Hg	200	< LoD	0.5
Rh	103	< LoD	0.2	Tl	205	< LoD	0.2
Ru	104	< LoD	0.2	Pb	208	< LoD	0.2
Ag	107	< LoD	1	Bi	209	< LoD	0.1
Pd	108	< LoD	0.2	Th	232	< LoD	0.1
Cd	114	0.3	0.2	U	238	< LoD	0.05

Conclusions

Trace contaminations in 7N high purity gallium phosphide can be determined reliably and routinely with the Element GD PLUS GD-MS without prior digestion.

While most analytes like Ti, Ba and La are resolved from interferences in medium mass resolution (R = 4000), high mass resolution (R = 10000) is required for Ag because of the GaAr interference. Sub-ppb detection limits, even for elements like Sb and Ge, are achieved by neglectable formation of triatomic interferences and reduced abundance sensitivity. That is enabled by the fast-flow source design and the reverse Nier-Johnson geometry.

Semiquantitative quantification of element concentrations can be performed without standard reference materials using the standard RSF factor approach. The high sensitivity of the instrument, the reliable separation of interferences in medium and high mass resolution, the outstanding peak stability, the low formation of interferences and the low abundance sensitivity enable limits of detection of 0.05 to 1 ppb for most elements.

The sum of all impurities in the GaP sample was below 50 ppb, implying that a purity of 7N GaP can be assessed with the instrument.

Safety considerations

Before handling GaP, please read the MSDS and follow the laws. Especially finely deposited GaP can react with moisture in air to form extremely toxic phosphine gas. Phosphine gas is reported to have a garlic-like or fishy odor[6]. Handle used cones, anode caps and flow tubes in a hood.

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