

# Investigation of Various GeF<sub>4</sub> Gas Mixtures for Improvement of Germanium Ion Implantation

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# OBJECTIVE

Evaluate various GeF<sub>4</sub> gas mixture compositions for improving germanium ion implantation performance.



 $GeF_4/H_2$  and  $GeF_4/CH_3F$  Co-flow (fixed ratios)

Fixed Source Beam at 20 mA



Beam Spectrum



Germanium implant is commonly used in advanced semiconductor device manufacturing as one of the major material modification steps. Germanium Tetrafluoride (GeF<sub>4</sub>) is almost exclusively used as the primary source gas and its impact on ion source performance (poor source lifetime due to fluorine-induced halogen cycle) is well known.

**TOOL / EXPERIMENTAL SETUP** 

All of the experiments presented in this poster were performed on an implant source test stand (STS) which is located at Entegris. In this test, an Indirectly Heated Cathode (IHC) source with tungsten (W) arc chamber and liners were used as this represents the most typical ion source configuration used in the field. During the beam current performance test, the beam current was normally run under the fixed source beam at 20 mA. Additional tests were run for certain conditions in which the arc current was fixed at 2 A, and these results are also presented in this poster. Other major beam parameters were set up as shown below unless noted otherwise:

- Arc voltage 90 V
- Extraction voltage 20 kV
- Suppression electrode voltage 3 kV
- Source magnet and electrode positions were optimized for each beam condition

\*Tests were run on different dates and times. A standard Ge<sup>+</sup> beam using pure GeF<sub>4</sub> was run every day to record the tool baseline condition. Beam currents were then normalized to that condition for comparison.

2.4

#### GeF<sub>4</sub> with Xe or N<sub>2</sub> co-flow

#### $GeF_4$ with $GeH_4$ or $H_2$ co-flow

\*  $GeF_4/H_2$  mixture had the same mixture percentage as the  $GeF_4 + CH_3F$  (High) condition and the equivalent amount of "H" as the GeF<sub>4</sub> + CH<sub>3</sub>/F (Low) due to 2 "H" in H<sub>2</sub> and 3 "H" in CH<sub>3</sub>F.

- Overall,  $GeF_4/H_2$  mixture had the highest beam current then followed by  $GeF_4 + CH_3F$  (High) and  $GeF_4 + CH_3F$  (Low) conditions.
- Both  $H_2$  and  $CH_3F$  could reduce the W<sup>+</sup> and  $WF_x^+$  beams due to the added hydrogen.
- The by-product of  $CH_3F$ , such as C<sup>+</sup> and  $CH_x^+$ , could be observed in the small insert chart.

### SOURCE CONDITIONS – 11 HOURS SHORT SOURCE LIFE TEST



- Overall the additional N<sub>2</sub> or Xe caused a negative beam current impact due to the dilution of the dopant species with the co-gas.
- Xenon caused a greater drop in Ge<sup>+</sup> beam current when co-flown with GeF<sub>4</sub> relative to nitrogen.

\* The GeF<sub>4</sub>/H<sub>2</sub> and GeF<sub>4</sub>/GeH<sub>4</sub> have the equivalent amount of "H" in each mixture. **A** 2.2 **8** 1.6 • GeF<sub>4</sub> Only ▲ GeF<sub>4</sub>+H<sub>2</sub> 1.4 ● GeF₄+GeH₄ 1.2 1.2 1.4 0.4 0.8 0.6 GeF<sub>4</sub> Gas Flow (sccm)

ArcV 90V, Source Beam fixed at 20 mA

- Both  $GeF_4/H_2$  and  $GeF_4/GeH_4$  showed ~14-15% in Ge<sup>+</sup> beam current over pure GeF<sub>4</sub>.
- GeF<sub>4</sub>/GeH<sub>4</sub> achieved the maximum beam current at a lower GeF₄ flow rate due to the additional Ge that is present from the inclusion of germane in the mixture.
- GeF<sub>4</sub>/GeH<sub>4</sub> co-flow generated ~2% higher peak beam current relative to that of  $GeF_4/H_2$
- After running the GeF<sub>4</sub>+GeH<sub>4</sub> combination there was a significant amount of residue observed in the source area due to decomposition of the germane. In subsequent tests, which did not include Ge containing gases, the Ge<sup>+</sup> beam peak was observed indicating that the residue was contaminating the beam.



EDS Analysis on Flake	Analysis on Flakes and Residues from Source (d) $GeF_4 + CH_3F$					
Location	C (at.%)	W (at.%)	F (at.%)	Ge(at.%)	0(at.%)	

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	Residue/coating Underneath base liner	71.86	23.76	0.26	0.06	4.06
		73.22	21.23	0.22	0.00	5.33
	Flake from anti-cathode	72.97	21.64	0.15	0.10	5.14



\* The GeF<sub>4</sub>/GeH<sub>4</sub> mixture had the equivalent amount of "H" as the GeF<sub>4</sub>/H<sub>2</sub> and GeF<sub>4</sub>/Ch<sub>3</sub>F (Low). Arc voltage is 90 V unless specified.

Test Condition	Cathode Weight Change (g/Hour)
Pure GeF <sub>4</sub>	0.415
$GeF_4/H_2$	-0.036
GeF <sub>4</sub> /CH <sub>3</sub> F (Low)	0.076
$GeF_4/CH_3F$ (High)	-0.044
GeF <sub>4</sub> /CH <sub>3</sub> F (High) ArcV 60V	0.043
$GeF_4/GeH_4$	-0.133

CONCLUSIONS

- Source (a) with  $H_2$  co-flow looked relatively clean.
- Due to the carbon content of the  $CH_3F$ , significant black carbon residue was observed in source (b), (c) and (d) especially on the liners facing the gas entry.
- Flakes and residues were observed in sources with CH<sub>3</sub>F and also highlighted in source (d). EDS analysis of the flakes and residue show a high carbon concentration which confirms the visual observations seen when running a co-flow of CH<sub>3</sub>F
- \*Note: Oxygen in EDS is commonly seen once the once the parts have been exposed to air.
- Co-flowing with hydrogen, GeH<sub>4</sub> or CH<sub>3</sub>F shift the cathode weight change to be negative; however

## GeF<sub>4</sub> with CH<sub>3</sub>F or H<sub>2</sub> co-flow



- In this test, the GeF<sub>4</sub> flow rate was fixed at 1 sccm and varying amounts of either  $H_2$  or  $CH_3F$ were co-flowed in order to test the impact on the beam current. Two beam control modes were tested - source beam at 20 mA or arc current at 2 A.
- In fixed source beam mode, Ge<sup>+</sup> beam was improved by ~17% by GeF<sub>4</sub>/H<sub>2</sub> and less than 5% by  $GeF_4/CH_3F$ .
- Under fixed arc current mode, Ge<sup>+</sup> beam was increased by ~17% by GeF<sub>4</sub>/H<sub>2</sub> and ~12% by  $GeF_4/CH_3F$ .

 $GeF_4/H_2$  is the most neutral, which is optimal, without any of the negative source life impact of using  $GeH_4$  or  $CH_3F$ .

- The test results presented in this poster comparing various  $GeF_4$  gas mixtures with a pure  $GeF_4$  base-line show the following:
  - Co-flow with inert gases, such as N<sub>2</sub> or Xe, generally reduces Ge<sup>+</sup> beam current.
  - GeH4 co-flow enables improvement in beam current, as does co-flow with hydrogen. However, during our test, significant Ge residue inside the source area was observed after running GeH₄ co-flow.
  - Co-flow CH<sub>3</sub>F results in higher Ge<sup>+</sup> beam current than pure GeF<sub>4</sub>. But the gain is less than  $GeF_4/H_2$  mixture.
  - Beam spectra show that  $CH_3F$  can also reduce the W<sup>+</sup> beam similar to co-flowing with Hydrogen. However, the addition of  $CH_3F$  results in C<sup>+</sup> and  $CH_x^+$  beam peaks being observed.
  - Due to the carbon content in CH<sub>3</sub>F, significant carbon residues are observed. Flakes or residues can be formed and accumulate in the arc chamber which can impact performance and/or source life. EDS confirmed those flakes/residues are mainly carbon.
- After testing the different co-gases of N<sub>2</sub>, Xe, GeH<sub>4</sub>, CH<sub>3</sub>F and comparing to the baseline of GeF<sub>4</sub>, it still clearly shows that the GeF<sub>4</sub>/H<sub>2</sub> mixture provides the highest beam current and longest source life performance.

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