

# Enhanced Life Ion Source For Germanium And Carbon Ion Implantation

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**Abstract.** Germanium and carbon ions represent a significant portion of total ion implantation steps in the process flow. Very often ion source materials that used to produce ions are chemically aggressive, especially at higher temperatures, and result in fast ion source performance degradation and a very limited lifetime [B.S. Freer, et. al., 2002 *14th Intl. Conf. on Ion Implantation Technology Proc., IEEE Conf. Proc.*, p. 420 (2003)].  $\text{GeF}_4$  and  $\text{CO}_2$  are commonly used to generate germanium and carbon beams. In the case of  $\text{GeF}_4$  controlling the tungsten deposition due to the de-composition of  $\text{WF}_6$  (halogen cycle) is critical to ion source life. With  $\text{CO}_2$ , the materials oxidation and carbon deposition must be controlled as both will affect cathode thermionic emission and anti-cathode (repeller) efficiencies due to the formation of volatile metal oxides. The improved ion source design Extended Life Source 3 (Eterna ELS3) together with its proprietary co-gas material implementation has demonstrated >300 hours of stable continuous operation when using carbon and germanium ion beams. Optimizing cogas chemistries retard the cathode erosion rate for germanium and carbon minimizes the adverse effects of oxygen when reducing gas is introduced for carbon. The proprietary combination of hardware and co-gas has improved source stability and the results of the hardware and co-gas development are discussed.

**Keywords:** ion implantation, ion sources, doping impurity implantation in germanium and carbon.

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## INTRODUCTION

Pre-amorphization implants (PAI) are becoming increasingly popular in CMOS processing as junction depths decrease. PAI and/or combining with co-implants are used to avoid channeling effects and inhibit the boron diffusion [2]. Carbon is now a standard co-implant species in the advanced logic MOSFET SDE implant sequence due to its reduction in primary dopant transient enhanced diffusion [3]. For decades the industry has suffered with shortened ion source lifetimes in the order of 20 hours when using  $\text{GeF}_4$  to implant Germanium. Attempts such as diluting the plasma with co-gases nitrogen [4], argon [5], argon or xenon [6] to sputter deposited W from the cathode have been marginal at best in extending source lifetimes. More exotic premixed co-gases such as 98.5wt% Xe/1.5wt%  $\text{H}_2$  [7] have also been tried but the  $\text{H}_2$  component was not optimized for the fear of creating excessive HF which can pose safety and equipment reliability concerns.

The Axcelis Eterna ELS2 source has been optimized to run all species of gas with source life ranging from 200 to 800 hours (energy and species dependent) with reduced gas consumption. As with all sources its lifetime performance was diminished when running dedicated Germanium ( $\text{GeF}_4$ ) and Carbon ( $\text{CO}_2$ ). To overcome this new challenge a two pronged approach would be required to simultaneously address all issues caused by running  $\text{GeF}_4$  and  $\text{CO}_2$  and still

meet the exemplarity performance of the ELS2 when running all other species.

Failure modes of  $\text{Ge}^+$  ( $\text{GeF}_4$ )

1. Cathode electron emission reduction due to increase in mass of cathode and cathode repeller due to the halogen cycle ( $\text{WF}_6$ )
2. Reduced extraction current due to the reduction in the arc slit width due to the halogen cycle ( $\text{WF}_6$ )
3. Formation of tungsten whisker and nodules on internal arc chamber liners and arc slit optics which break off and cause shorts on the anti-cathode
4. Coating and failure of key ion source insulators with W and  $\text{C}^+$  due to the formation of  $\text{WF}_6$  and  $\text{CF}_x$
5. Coating of key extraction electrode insulators with  $\text{CF}_x$

Failure modes of  $\text{C}^+$  ( $\text{CO}_2$ )

1. Reduced thermionic emission of the cathode (poisoning)
2. Change in the emissivity of the arc chamber as it coats with a layer of carbon and or oxide
3. Oxidation of cathode repeller – failure to repel electrons
4. Coating of key ion source insulators with carbon from  $\text{C}^+$  and  $\text{CF}_x$
5. Oxidation damage to the refractory metal main arc chamber body (non-consumable)

As the failure modes are quite different between these two species understanding the failure mechanisms and the subsequent changes in the internal arc chamber components over time cathode are critical to implementing a universal solution.

The Eterna ELS3 source is a direct result of such efforts and addresses the source hardware failure modes of both CO<sub>2</sub> and GeF<sub>4</sub>. It was also determined that a second approach was also needed to control the dopant gas ionization by products of O<sup>-</sup> and F<sup>-</sup>.

For Ge, up to two co-gases were added to control the halogen cycle where one acts as reaction gas to tie up the F<sup>-</sup> and the second as a sputter gas to address any remaining build up of tungsten on the cathode or repeller surfaces. For carbon, a co-gas was added as reaction gas to deal with the carbon poisoning and oxidation issues.

Two germanium tests are reported here, one with hydrogen co-gas where normal cathode erosion is observed and source life can be predicted by monitoring the cathode heating power slope over time [8]. The erosion rate of the cathode is estimated as ~1.43 E20 atoms/hr from this study.

The second test using co-gases of hydrogen and a noble gas to sputter the cathode we are able to reduce the cathode material loss by adding back tungsten by fine tuning the halogen cycle (WF<sub>6</sub> decomposition). The rate of cathode erosion is greatly reduced as evidenced by the cathode heating power curves.

When running CO<sub>2</sub> the carbon deposition onto arc chamber components alters the tungsten cathode thermionic emission efficiency. The formation of tungsten carbide (WC<sub>x</sub>) [9] and lemon yellow volatile tungsten oxide (WO<sub>3</sub>) and conductive coatings on key source insulators are detrimental to the source stability and lifetimes.

Proprietary gas chemistries in conjunction with hardware improvements are key to the success of the Eterna ELS3 ion source for Axcelis High Current implanters. Source life is extended by an unprecedented 300% for Germanium and Carbon applications used for shallow junctions in sub 2X nm nodes. In keeping with green initiatives and customer cost concerns, when GeF<sub>4</sub> is run at the recommended flows gas consumption is ~ 0.5 gm/hr.

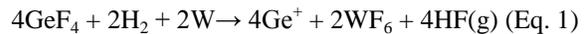
## EXPERIMENT

After the co-gases were selected, the ion beams were tuned to their optimal levels. This involved complex interactions between primary and co-gas gas flow levels and arc chamber electrical settings. The implant system ion mass spectrum analyzer was used to determine what ion fragmentations were being

produced. Arc chamber component erosion and or re-deposition profiles noted and weights were taken at the completion of each test to aid in determining optimal hardware design and plasma chemistries. All primary and co-gases were independently installed and controlled as part of design of experiment. The extraction current, beam current, source parameters and beam stability were carefully recorded during the source life testing. Ion beam spectra are taken at different stages of the tests.

## RESULTS AND DISCUSSION

Normal source life is limited to the amount of cathode material available to support thermal evaporation, sputtering and any chemical etching taking place in the arc chamber. For Germanium, the chemistry and kinetics can be written as the follows:



$$\text{Reaction Rate} \propto A[\text{P}_{\text{WF}_6}]^{-0.9}[\text{P}_{\text{H}_2}]^{0.5}\exp[-E/RT] \quad (\text{Eq. 3})$$

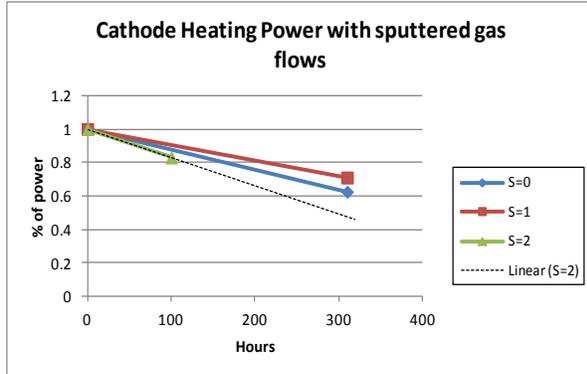
Eq. 1 shows the formation of WF<sub>6</sub> which drives the halogen cycle

Eq. 2 shows how H<sub>2</sub> co-gas reduces the WF<sub>6</sub> into W and 6HF and ties up available F<sup>-</sup>

Eq. 3 shows that the reaction rate is proportional to the partial pressure of WF<sub>6</sub> and H<sub>2</sub> at a given working temperature.

With limited feed GeF<sub>4</sub> flow (in a few sccm) to the arc chamber, up to 1mA of HF is extracted during the Ge<sup>+</sup> operation. This translates to ~1.2E16 molecules/sec of HF which is around 30 ppm. This is a trace amount in comparison to other high flow CVD processes with several liters per minutes. F<sup>-</sup> from GeF<sub>4</sub> etches W liners to form tungsten fluorides; on contact to the hot cathode tungsten fluoride decomposes, depositing W on the cathode and returning F<sup>-</sup> to plasma only to continue the cycle. The increasing mass of cathode rails the power supply, thermionic emission drops, arc current drops and the beam current then drops below the required setpoint. In order to defeat/control the halogen cycle the primary and co-gas flows were optimized.

Figure 1 shows the process optimization using H<sub>2</sub> co-gas with and without sputtering co-gases. The gas ratio for GeF<sub>4</sub> and H<sub>2</sub> is held constant for each condition.



**FIGURE 1.** Optimization of sputtering gas. S=0 has no sputtering co-gas, S=1 shows the sputtering co-gas in an optimized state. S=2 shows the sputtering co-gas was set too high and resulted in premature source failure (100hrs).

The halogen cycle can be interrupted with the presence of a reducer gas, The proprietary co-gases are used to tailor the balance of mass transport within the ion source. In both cases, there is no evidence of the cathode mass increasing. Eq.(2) is the  $WF_6$  decomposition to W in the presence of  $H_2$  at elevated temperatures.

S=0 (GeF<sub>4</sub> + H<sub>2</sub>): No sputtering co-gas

This recipe was very telling due to the absence of noble gas. Without the addition of noble gas to sputter tungsten from the internal arc chamber components there was parity between the sputter yield of tungsten from Ge+ and the H<sub>2</sub> cogas reducing the  $WF_6$  into 6HF. This parity effectively neutralized the halogen cycle and the cathode eroded at a rate similar to non-fluorinated gas species. As evidenced from the cathode heat power curve the slope is greater than that of the S=1 indicating the cathode eroding at a higher rate thereby shortening source life. The reduced rate of  $WF_6$  formation (less available F<sup>-</sup>),  $WF_6$  decomposition and subsequent W depositing back onto the hot cathode was also reduced. Per Eq.3 the lower partial pressure of  $WF_6$  ( $P_{WF_6}$ ) results in a reduced reaction rate.

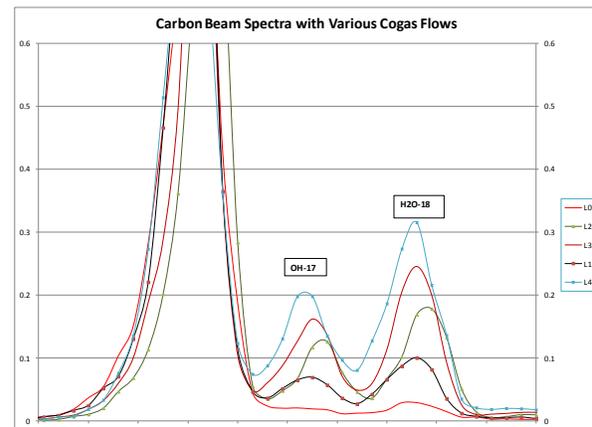
At the end of test, the cathode was weighed and had lost 13.1 grams after 300 hours of run time. The remaining weight was 62.5% of its original which corresponds to a 28% reduction in heating power. This calculation corresponds to the delta observed S=0 and S=1 curves at the 300 hour mark.; i.e.; 2.1% of less heating power to 1 gram of cathode mass reduction. The tungsten has 3.276E+21 atoms/gm and the loss of cathode material (erosion rate) is 0.043667 gm/hr which corresponds to 1.43E+20 atoms/hr.

S=1(GeF<sub>4</sub> + H<sub>2</sub> + noble gas): with sputtering co-gas: The noble gas sputtered yield of tungsten is ~1.05 atom/ion [10] results in more tungsten available to react with F<sup>-</sup>, which leads to the increased formation of  $WF_6$  and takes the source out of halogen cycle

equilibrium when compared to S=0. The higher reaction rate leads to more halogen redeposition onto the cathode surface so that the cathode mass reduction is slower by 0.013492 gm/hr or 4.42E19 atoms/hr, as indicated S=1 in the Fig. 1.

Per S=1, More tungsten sputtered from cathode due to the presence of the inert gas increases the rate of  $WF_6$  formation leading to higher  $WF_6$  partial pressures in the arc chamber; the reported apparent activation energy of this process of Eq.(3) is 64-70±5 kJ/mole which is favorable in temperature ranges of 300–800°C [11]. The  $WF_6$  molecule does not decompose spontaneously on the tungsten surface, hydrogen serves as reducer to strip the fluorine radicals from  $WF_6$ . The molecules chemisorbs on the tungsten cathode surface increasing its mass over time [12].

It can be observed that in case S=0 the cathode heat power was reduced by 62.5% and for case S=1 a 71% reduction over the duration of the test.

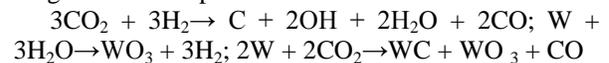


**FIGURE 2.** CO<sub>2</sub> cracking pattern with multiple cogas flows

#### Carbon ion beam operation:

Carbon ion beam generation has several issues that the industry has struggled with for a long time. Carbon changes the work function of the cathode by forming a carbide resulting in reduced electron emission for a given cathode power setting and the local oxidation of key internal arc chamber components due to the presence of oxygen from the primary dopant gas CO<sub>2</sub>. By introducing hydrogen cogas to the CO<sub>2</sub> recipe the adverse effects of the oxygen can be neutralized as the O<sup>+</sup> is converted to <sup>17</sup>OH, <sup>18</sup>H<sub>2</sub>O. Reviewing Figure 2 where all recipes parameters are held constant and the H<sub>2</sub> flow is increased in fixed increments until beam current is impacted and or saturation of the <sup>17</sup>OH peak.

The possible chemical reactions that affect the tungsten cathode performance are as follows:



The lemon yellow residuals observed near the cathode side of the arc chamber suggests that the formation of  $WO_x$  occurred during the source operation. The major product of the oxide formed has a stoichiometry of  $WO_{2.7}$ , which indicates that both  $WO_3$  and  $WO_2$  phases are present. Per the following equations the ratio of  $CO_2$  to  $H_2$  needs to be optimized to minimize the negative effect of arc chamber component oxidation.

The thermodynamic and kinetics of the  $WO_3 \leftrightarrow W + 3O$  reaction that occurs when the concentration of oxygen ( $C_O$ ) corresponds to  $1/3^{rd}$  order of the partial pressure of  $WO_3$ . The equilibrium constant  $K$  as shown below in equation (4) [13]

$$C_O = p_{WO_3}^{1/3} \cdot K \quad (\text{Eq. 4})$$

Careful consideration also was given the choice of materials used the proximity of the IDH cathode. In the case of Eterna ELS3 graphite has improved the oxidation resistance. The oxidation probability of graphite is 0.45 at  $P_O=10^{-3}$  torr at  $800^\circ\text{C}$  [14] which is high. Proprietary materials and seals were used to prevent the leakage of gases to prevent premature failure of components external to the arc chamber.

Based on the two tests results, we have confirmed the role of sputtering co-gas in the erosion rate of the cathode and subsequent long life source operation for  $Ge+$  ion beams.

## CONCLUSIONS

We have demonstrated an ion source design that delivers unprecedented levels of source life to provide higher tool uptime and significantly lower cost of ownership for Germanium and Carbon implants. Through the careful selection of arc chamber materials the improved ion source design the Eterna ELS3 together with its proprietary co-gas material implementation has extended source life by an unprecedented 500% for Carbon and a 300% improvement for Germanium applications. To make this possible the utilization of the cathode had to be improved, the highly reactive by-products of ionized primary gas dopants had to be controlled ( $WF_6$  and  $O$ ), and all critical source electrical insulators had to be protected from etching or coating with conductive materials. The use of mass spectrometry when tuning the process recipes was critical to controlling the detrimental effects of ionizing  $GeF_4$  and  $CO_2$ .

## ACKNOWLEDGMENTS

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