Exemplary Ion Source for the Implanting of Halogen and Oxygen Based Dopant Gases

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Abstract: **The demand from device manufacturers for longer source life, increased beam currents, beam stability and non-dedicated species operation has pushed the present ion source design to its limits. Each of the above requirements is not mutually exclusive and usually one or more performance characteristics are typically sacrificed so as to ensure the ion source does not fail prematurely. The highly corrosive nature of fluorides and oxides generated from cracking GeF_4, BF_3, SiF_4, CO, and CO_2 challenges the traditional refractory metals used to construct the ion source. The formation of tungsten fluorides (WF_x) which then decompose (halogen cycle) and deposit tungsten onto critical heated surfaces such as the cathode, repeller (anode) and arc slit optics degrades source performance. The WF_x will also react with the critical source insulators, forming a conductive coating that also causes beam instabilities and shortened source lifetimes. The formation of WO_2/WO_3 on the internal source components negatively impacts transitions to other species such as ^{11}B and $^{49}BF_2$ until the residual oxygen released from the tungsten oxides is below some threshold level.**

The use of lanthanated tungsten for internal arc chamber components in many cases does not require the use of a co-gas such as hydrogen to tie up residual fluorine and/or oxygen to prevent the aforementioned ion source damage. The reaction of F^- and O^- with lanthanum results in a protective surface layer which is very stable at temperatures >2000°C, whereas tungsten fluorides and oxides are very volatile (halogen cycle) and lead to shorter source life and increased ion beam instabilities. Other important attributes of this source are improved cathode electron emission due to its lower work function and decreased formation of tungsten carbide on the cathode tip which will reduce cathode electron emission for carbon implants.

This new alloy coupled with the patent pending Axcelis co-gases and improved cathode repeller seals will further improve source stability and ensure predictable, repeatable, and longer source lifetimes.

Keywords—lanthanum-oxide doped tungsten ion source; halogen cycle; tungsten; Ion implantation, Ion Sources, Doping Impurity Implantation

I. INTRODUCTION

The halogen decomposition from germanium tetra fluoride and other fluoride base dopant gases has been a perpetual problem ever since the introduction of Bernas and IHC ion sources constructed from traditional refractory materials such as tungsten, molybdenum and tantalum. When running fluorine based dopant gases the formation of volatile tungsten hexafluoride and its subsequent decomposition back into tungsten metal when coming into contact with high temperature surfaces (>400°C) wreaks havoc on ion source lifetime and stability. Tungsten deposition onto the cathode results in an increase in the power required to maintain arc current and eventually forces the servo system into saturation and causes beam instabilities. The deposition of tungsten into the arc slit optics reduces its width over time driving up the required arc power to maintain the require extraction current for a given recipe. The increase in arc power increases the sputter rate of the cathode and repeller reducing their lifetimes, but also increases the quantity of available tungsten to react with fluorine thereby feeding the halogen cycle. Material is also deposited into the arc chamber liners and where it may delaminate causing cathode and repeller arcing. As with most technologies, evolution has progressed in stages where for decades work arounds such as timer purges were used in an attempt to sputter off deposited tungsten or controlling how long to run these dopants before switching to another species to mitigate the damage.

As plasma chemistries were analyzed and understood, other methods of controlling the halogen cycle were developed. One method of controlling the deleterious effects of the fluoride and or oxides formed when cracking the primary dopant has been to introduce hydrogen and or a hydride based secondary gas to chemically react out these corrosive volatile by products. In some cases a secondary gas such as phosphorous hydride or fluoride can be added to tie up residual oxygen, or in the case of a fluoride based dopant the other gas may be hydrogen or a hydride based secondary gas. The introduction of these secondary gases can interfere with the ionization of the primary dopant which may reduce the overall ion beam current or the by-product of cracking the primary dopant in combination with the secondary gas may result in energetic cross contamination. As with all new techniques, tradeoffs in performance may occur and hopefully any new problems introduced are less complex to solve than the initial concern.

With the recent advent of high dose "material modification" implants such as germanium, silicon and carbon combined with the industries reluctance to dedicate tools for specific processes alternate approaches to maintaining source stability with improved lifetimes is required. One such approach which can be used alone or in conjunction with the aforementioned co-gases is to construct the internal arc chamber components from a fluorine/oxygen resistant alloy such as La_2O_3-tungsten (lanthanated tungsten).

II. EXPERIMENTAL

An Axcelis ELS2 ion source was assembled using WLa in place of tungsten for any internal component that was exposed to the plasma. Each of the following recipes were run for 10 hours each in the following sequence: SiF_4, GeF_4,

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BF_3, CO_2 and CO. All ion source parameters were monitored and the ion source was opened and visually inspected after each 10 hour run. None of the components were replaced or cleaned between each test.

III.   RESULTS AND DISCUSSION

Typically an indirectly heated cathode is constructed from tungsten which has one of the highest melting temperatures, but it also has one of the highest work functions at 4.5 eV. This is of special interest when using oxygen based dopants where the work function of the cathode is increased to the point that electron emission is reduced resulting in a loss of ion beam currents. The introduction of lanthanum into the cathode decreases the work function to 3.3 eV[1,2] and substantially increases emission current densities to 4 A/cm^2 at 1900K when compared to pure tungsten at 2300 K with only one hundredth of the emission current [3]. For the remaining arc chamber components a protective film of LaF_3 or La_2O_3 is produced and is thermally stable up to 1490°C [4] and 2300°C, respectively. As the $WLaO_3$ resides in the tungsten grain boundary it will continue to diffuse to the surface and replenish the protective coating. This in turn reduces the formation of volatile refractory gases. When lanthanum is either sputtered, etched or evaporated into the arc chamber plasma which contains tungsten, oxygen or fluorine it does not form a highly reactive and unstable compounds such as MoF_x, WF_x, and TaF_x , instead it forms a stable oxide or fluoride compound that is also deposited onto the interior arc chamber surfaces further improving the protective coating. This material attribute is also important when CO_2 or CO is used as a process gas and the cathode work function increases due to the presence of oxygen in the plasma [5].

Fluoride based dopants (GeF_4 example)

The following is a comparison of standard W arc chamber components vs. co-gas enhancement vs. WLa alloy components. It should also be noted when running other fluorine based dopants that the chemistries are also applicable.

GeF$_4$ with Tungsten Components and no Cogas:
$3 GeF_4 + 2W \rightarrow 3Ge^+ + 2WF_6$ (g) Dopant cracking & halogen cycle starting (1)
WF_6 (g) $\rightarrow$ W(s) + 6 F(g) Decomposition with W deposition (2)
$6F + W(s) \rightarrow WF_6$ Halogen cycle continuation (3)
Eq.1 shows that 1 mole of GeF_4 produces 2/3 mole of WF_6 which in turn feeds the reactions from Eqs.2 and 3. Note the heavy tungsten deposits on the cathode/repeller and etching of the liners, as shown in Fig. 1.

Improved chemistry for GeF$_4$ with Tungsten Components + H$_2$ Co-gas [6]:
$4 GeF_4 + 2H_2 + 2W \rightarrow 4Ge^+ + 2WF_6$ (g) + 4HF(g) (4)
$WF_6 + 3 H_2 \rightarrow W + 6 HF$ (5)
$2 W + 3 GeF_4 + H_2 \rightarrow W + 3 Ge^+ + 6 HF + WF_6$ (6)
Eq. 4 shows the improved chemistry where 1 mole of GeF_4 produces 1/2 mole of WF_6 and 1 mole of HF (an *in-situ* chemical etchant) resulting in no tungsten deposition (no halogen cycle) or etching of the liners, as shown in Fig. 2.

Metallurgical improvement for GeF$_4$ using WLa components + no Co-gas:
$3 GeF_4 + 4 WLa \rightarrow 3 Ge^+ + 4 \underline{LaF_3 \ (s)} + 4 W$ (7)
$2GeF_4 + H_2 + 2 WLa \rightarrow 2W + 2Ge^+ + 2 \underline{LaF_3}(s) + 2HF(g)$ (8)
As LaF_3 is high temperature stable compound there is no WF_6 formed with no tungsten deposits on the cathode & repeller (no halogen cycle) or etching of the liners, as shown in Fig. 3.

Fig. 1. Halogen cycle/tungsten deposition after 70 hours of GeF$_4$

Fig.2. Ion source after 300 hours of GeF$_4$ and H$_2$ Co-gas

Fig. 3. Ion source after 50 hours of SiF_4, GeF_4 and BF_3 using WLa components & no H_2 co-gas.

Oxygen based dopants for carbon implants (CO_2 and CO example)

Carbon has emerged as a widely used dopant in the semiconductor industry for a variety of material modification applications such as inhibiting diffusion of co-dopants or enhancing stability of the doped region. In this regard, carbon dioxide (CO_2) and carbon monoxide (CO) are two commonly used dopant gas sources for carbon implantation. The residual oxygen from the disassociation of the carbon molecule will oxidize the chamber liners, but most notably it will damage the cathode shield causing a premature failure of the ion source (Fig. 4).

Due to the high temperature of the cathode shield, most notably the area across from the filament (mounted inside the cathode) the shield will eventually break into 2 pieces.

One method to address this issue is to use a "gettering" co-gas such as PH_3 to react out as much O^{2-} as possible before negatively impacting ion beam current. The formation of phosphorus oxides P_4O_6 and P_4O_{10}, which have low melting points at 23.8°C and 422°C [7] (vapor phase) allows them to be pumped out. This is critical near the cathode shield which is the hottest component other than the cathode. As with any technique there can be secondary effects, in this case a reduction in available oxygen will reduce the formation of

**Table 1: Optima HDx Trace Metal Results by VPD ICP-MS**

	SURFACE CONCENTRATION (x 10^{10} atoms/cm^2)			
	Detection Limit	BF2+_no cogas	BF2+ _cogas	Control
Al	0.1	1.7	1.9	<0.1
La	0.001	0.097	0.2	<0.001
W	0.0005	4.5	2.4	<0.0005

hydrocarbons (can be pumped out) resulting in increased carbon deposits. When using this technique one must balance the cathode shield oxidation rate and carbon deposits. The introduction of WLa components will reduce the cathode shield oxidation rate and PH_3 co-gas flow which then increase the formation of hydrocarbon.
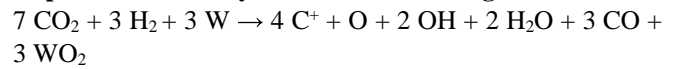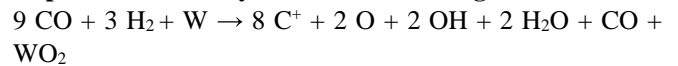
CO_2 with W components no co-gas:

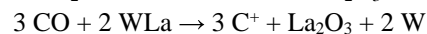$4 CO_2 + 3 W \rightarrow 4 C^+ + WO_2 + 2 WO_3$

Carbon CO along + W:

$5 CO + 2 W \rightarrow 5 C^+ + WO_2 + WO_3$
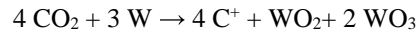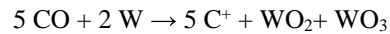
Improved Chemistry for CO_2 with H_2 co-gas:

$7 CO_2 + 3 H_2 + 3 W \rightarrow 4 C^+ + O + 2 OH + 2 H_2O + 3 CO + 3 WO_2$

Improved Chemistry for CO with H_2 co-gas:

$9 CO + 3 H_2 + W \rightarrow 8 C^+ + 2 O + 2 OH + 2 H_2O + CO + WO_2$

Metallurgical improvement for Carbon using WLa components + no Co-gas:[8]

$3 CO_2 + 4 WLa \rightarrow 3 C^+ + 2 La_2O_3 + 4 W$

$3 CO + 2 WLa \rightarrow 3 C^+ + La_2O_3 + 2 W$
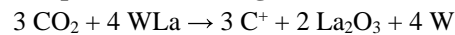
Steppng down the above list of equations each condition forms less WO_2 than the previous one, ending with WLa where no WO_2 is formed.

Metal Contamination for Fluoride based dopants:

A VPD ICP-MS trace metals test was performed using an Optima HDx with the following recipe: 14keV BF_2, 12mA, 5E15 implant with and without Kr/Hydrogen co-gas. Per Table 1 only a trace amount of lanthanum at 9.7E8 atom/cm^2 is observed with no co-gas and 2E9 with co-gas on. The tungsten level is reduced by ~50% with the co-gas on but at a higher level than the lanthanum. With the recent advances on the Purion H and its patent pending "5S" energy the filtration beamline, the lanthanum is in the non-detectable range while only trace amounts of tungsten is is observed for a BF_2 implant (table 2).

Fig. 4. Photo of a tungsten cathode and its corresponding tungsten cathode shield (tubular member that covers the cathode) after running CO_2 for 20 hours

Table 2: Purion H Metal Results by VPD ICP-MS

| | SURFACE CONCENTRATION (x 10^{10} atoms/cm^2) | | |
	Detection Limit	BF2+_no cogas	BF2+_cogas	Control
Al	0.1	2.4	0.47	0.25
La	0.001	<0.001	<0.001	n/a
W	0.0005	0.00055	0.00081	<0.0005

The erosion of the arc chamber gas inlet by fluorine based dopants such as GeF$_4$, SiF$_4$, or BF$_3$ can also affect the quantity of volatile WF$_6$ produced. This may contribute to an increase in the halogen cycle observed in the ion source, but may also increase the amount of these metals transported down the beam line. Using GeF$_4$ as an example it is thermally stable up to 1000°C, but with the presence of H$_2$ co-gas its thermal decomposition is altered when the gas phase molecules react on various surfaces with hydrogen based co-gases reducing its decomposition temperature to ~500°C. This reduces the activation and reaction energies. Again the use of a WLa to construct a gas input liner or constructing the entire arc chamber body from the alloy a protective LaF$_3$ layer forms which is stable up to 1490°C.

IV. SUMMARY

With the increasing use of material modification species such as high dose GeF$_4$, SiF$_4$, CO$_2$ and CO as well as conventional B11 and BF$_2$ recipes, the deleterious effects of the fluorine and oxygen by-products has shortened source lifetimes, increased ion beam instability and raised levels of metal contamination. To maximize productivity beam currents are typically increased to 80% of maximum which requires higher gas flows and arc powers, all of can have the aforementioned negative effects. From this study we have demonstrated that metallurgy (WLa) is also another tool that can be used in conjunction with Axcelis technologies patent pending co-gases, improved beamline filtration (Purion H) and the recently introduction of the extended life/reduced gas usage ELS4.

Fig.5. Erosion of the process gas inlet for a W arc chamber body after running dedicated GeF4 for >2000 hours

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