Improved Ion Source Stability Using H_2 Co-gas for Fluoride Based Dopants

Tseh-Jen Hsieh[1], Neil Colvin
Axcelis Technologies, Inc.
Beverly, MA 01915 U. S. A.
Tseh-jen.hsieh@axcelis.com

Abstract— Fluoride based gases are commonly used in the ion implantation. Gases such as GeF_4 and SiF_4 are used as pre-amorphization species and BF_3 is used for high dose BF_2 and ^{11}Boron p-type implants. These can be a productivity challenge for conventional ion implanters used for semi-conductor device applications. As device geometries continuously shrink, there is a trend to deliver higher beam currents at lower energies, with a corresponding reduction in particles and metal contamination.

A major issue is the ion source and extraction electrode discharging which is commonly referred to as glitching. This unintended interruption in the beam transport results in the ion beam sweeping or modulating and is typically associated with an increase of particles transported to the wafer. When this beam instability occurs for an extended period of time, the wafer must be re-implanted in the area which was under dosed. When the instabilities reach an unacceptable level the tool must be removed from production and the source components replaced, increasing the tool's cost of ownership. A third issue is the contamination of the wafer with material from the ion source. Fluorinated source gases are quite corrosive due to the formation of free fluorine radicals (F^-) during the fragmentation process. Refractory metal fluoride compounds are highly volatile and thus easily contact the internal components of the ion source chamber and the extraction optics assembly. To further exasperate source instability, these free fluorine radicals lead to the perpetuation of a halogen cycle where the cathode and repeller masses may be increased and the arc slit width may be reduced. Extraction of these F^- radicals from the ion source through the graphite extraction optics also forms CF_x vapors which surround the optics assembly, coating critical insulators which in turn cause beam instabilities.

The purpose of this work was to introduce a co-gas which would tie up these fluorine radicals and minimize their adverse effects on source components. H_2 was chosen as it captures free fluorine radicals once they form in the arc chamber plasma as HF_x and will also act as a reducer of WF_6 when it is formed. Other positives of H_2 are that it is relatively inexpensive, non-toxic, relatively safe to handle and chemically a good match with fluoride based gases. Earlier works have demonstrated the benefits of using H_2 co-gas when operating GeF_4 [1]. When two BF_3 molecules decompose they yield six fluorine radicals. Similarly, three hydrogen molecules decompose to six hydrogen ions. Testing on Axcelis multi-wafer and the single wafer Optima High Current tools has demonstrated improved ion beam stability (50x reduction in glitches for BF_2) which can translate into decreased particles and improved ion source life (200 to 300 hours for dedicated BF_2).

Keywords— Ion implantation, Ion Sources, Doping Impurity Implantation.

PACS: 85.40.Ry

[1] Author to whom correspondence should be addressed:
tseh-jen.hsieh@axcelis.com
978-787-9586

I. Introduction

It has been shown [1] that the common fluoride compounds such as GeF_4 and SiF_4 used for pre-amorphization (PAI) species and BF_3 as a source gas for B_{11} and BF_2 P-type dopant create problems not only for ion source operation but also impact device performance.

In recent years significant advances have been made in the development of high mass molecular (HMM) beam sources for dopant implantations into silicon. The driver for the development of these sources has been the need for very low energy implants where energy is partitioned between the atoms of a molecule in direct proportion to their mass. BF_2^+ is the most the widely used molecular ion with an atomic mass of 49 and has a single boron atomic mass of 11 that result in equivalent implant energy of 49/11[2]. This allows higher energy implants with improved beam transport efficiencies and also suppresses boron diffusion during the anneal step [3].

At the gate edge where BF_2 is used for several implants such as Source-Drain Extension (SDE), Source-Drain (SD), PAI, co-implanted species, halos and pockets, small variations in any one of these can lead to unacceptable fluctuations in device performance. The precision required to perform these implants therefore becomes critical. As an example, diffusion in SDE and halo implant is strongly influenced by damage generated during SD implantation, the understanding of defect generation as a function of beam characteristics of the ion implanter is critical in the process integration of advanced devices 65nm and beyond.

This study investigates the characteristics of BF_3 when it is ionized and the positive effects of using hydrogen as a co-gas. The quantity of hydrogen fluoride (HF_x) formed during the recipe optimization is aided by monitoring the AMU spectra and required dopant beam current level. The production and extraction of these F^- radicals from the ion source and through the graphite extraction optics forms CF_x vapors which will encompass the entire optics assembly attacking/coating critical high voltage insulators causing beam instabilities.

The production of HF is the result of the H^+ and F^- reaction in the ion source plasma which reduces the probability of free fluorine radicals attacking the materials from which the ion source/extraction electrode is constructed (tungsten, graphite, molybdenum, Al_2O_3). Due to the formation of these unwanted fluorine based radicals (WF_6, CF_x, AlF_x) system design may not always prevent damage to critical source components and the mass resolution of the bending magnet with a resolving aperture may not have a resolution of 1 amu to exclude contaminants such as CF_2, (amu 50). These radical gas compounds may also lead to increased wafer contamination over time as they transport and deposit down the beam line.

Formation of WF_6 in a high temperature vacuum environment (arc chamber) permits the halogen cycle to promulgate which further shortens source life and stability. Controlling the amount of free F^- can translate into reduced glitching, wafer repaints, improved source life and metal contamination.

II. EXPERIMENTAL

The design of experiments was conducted in two parts using the same tool where a baseline test without the co-gas was performed and after rebuilding the source and electrode the only variable changed was the addition of a previously optimized hydrogen co-gas flow. The GSD 200 E2 was used to conduct the tests using a customer's high volume production BF_2 recipe. The beam recipe was tuned without the hydrogen co-gas, and then the H_2 flow was optimized with regards to the amount of HF_x formed and effect on the required beam current as shown in Figure 1. The beam AMU spectra experiment indicates that the amount of HF_x will reach a maximum and then saturate for a given H_2 flow at a given set of beam tuning parameters.

III. RESULTS AND DISCUSSION

The fluoride based dopant gases generate free fluorine radicals during ionization in the arc chamber cavity. The high chemical volatility of refractory fluorides at the operating temperatures has proven not only to be detrimental by etching ion source refractory metals, electrode graphite but also causing the erosion of strike plates for off energy species located in the AMU beam guide (downstream of the ion source).

Regardless of what refractory metals are used to construct the arc chamber liners, thermal evaporation, sputtering, plasma and chemical etchings are several methods of converting refractory metals to the vapor phase. In the confines of the plasma charge neutrality is preserved and the specific density of fluorine radicals will react with tungsten ions to form WF_6 with a melting point of 2°C[4], as it is volatile it will decompose on heated surfaces as part of the halogen cycle. Due to the difference in ionization efficiency of GeF_4 and BF3, the electro-negativity of Ge is 1.8 and F is 4.0 (delta = 2.2) and B is 2.0 (delta = 2.0), respectively [5]. The greater the difference in electronegativity, the higher the ionization efficiency is expected. This is explains why the halogen cycle for BF3 is less severe than GeF_4. One would think that the first step in reducing available W is to develop a recipe where the arc voltage is as low as possible for a given recipe as the sputter rate is proportional to the voltage, as shown in Figure 2, but it is a double edged sword as optimal beam current requirement may not be met. The reduced sputter rate of the cathode may exasperate the effects of the halogen cycle requiring higher H_2 flows, but then again the formation of HF_x may be at it saturation and increased H_2 flow will have no effect.

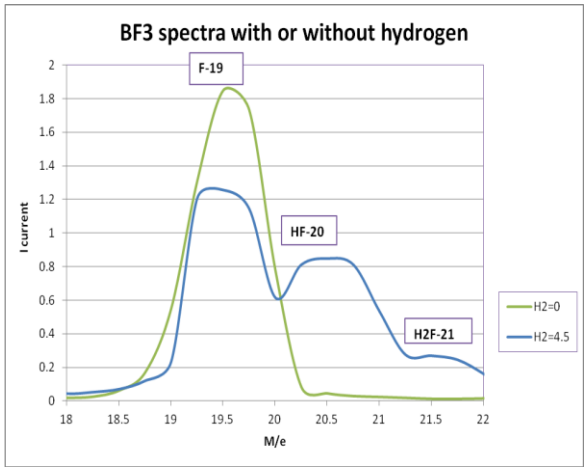

Figure 1: Beam Optimization with and without Hydrogen Co-gas.

To deal with this problem, the key is to reduce the available free fluorine radicals that lead to the halogen cycle. Under the ionization plasma condition there are equal amounts of positive ions and negative ions in the free space within the arc chamber. The positive ions are B^+, BF_2^+, Si^+, Ge^+, etc. and the negative ions are F^-. By introducing a pre-determined amount of hydrogen gas into the ionization chamber the highly reactive hydrogen ions (H^+) will combine with fluorine ions forming the chemical compound hydrogen-fluoride (HF_x). This reduction in WF_6 will not only prolong the life of the refractory metal components, but also reduce amount of doubly charged WF_6^{++} that can be transported down to the beam line to the wafer surface. Secondly, the trace amount of HF_x will chemically etch residuals within the ion chamber inner surfaces and as it is passes through the extraction electrode apertures it will chemically etch those surfaces as well as any adjacent insulators (known as *in-situ* chemical cleaning).

GeF_4 Reaction Model: (with/without the presence of H_2 co-gas)

$$GeF_4(g) + 2H_2(g) \rightarrow Ge^+(s) + 4HF^-(g) \quad (1)$$

Or:

$$GeF_4(g) \rightarrow Ge^+(s) + 4F^-(g) \quad (2)$$

Or:

$$WF_6(g) \leftrightarrow W^+(s) + 6F^-(g) \quad (3)$$

As noted throughout this paper these free fluorine radicals

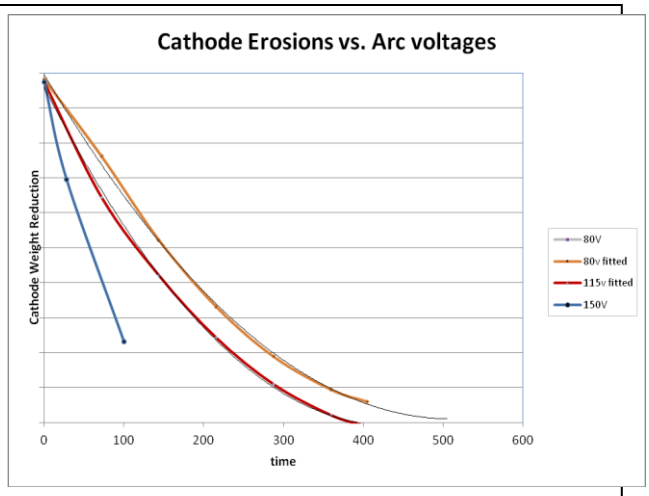

Figure 2: Cathode Erosion vs. Arc Voltage Curves

attack tungsten surfaces to form WF_6. H_2 works out to be a terrific choice as a co-gas to capture free fluorine radicals once they form in the arc chamber plasma. Hydrogen is relatively inexpensive, non-toxic, highly reactive but relatively safe to handle. When one GeF_4 molecule decomposes, two hydrogen molecules (forms four hydrogen ions) are needed to chemically react with the four fluorine ions, as shown in eq.(1). Whether tying up free fluorine when the dopant is cracked or if the halogen cycle releases fluorine back in to the plasma the H_2 co-gas will minimize the quantity of tungsten consumed.
The approach has shown good beam stability, source lifetimes and minimal de-lamination of coatings in the arc chamber. Stable glitch free beams typically translate into lower overall particle performance.
The beam spectrum scan is a built in feature for most ion implanters and is used to demonstrate how much of the ionized material at selected m/e was extracted and transported to the beam Faraday and to verify composition of the extracted ion beam by displaying off energy ions. By introducing the hydrogen as a co-gas to the BF_3 plasma, the chemistry changes completely because hydrogen is a strong reduction agent that reacts with the fluorine radicals, as indicated in equations (3) and (4) and (5).

$$4BF_3(g) + 3H_2(g) \rightarrow B + F + BF + 2BF_2 + 6HF(g) \qquad (4)$$

$$WF_6(g) + 3H_2(g) \rightarrow W^+(s) + 6HF^-(g) \qquad (5)$$
(With the presence of co-gas)

To form WF_6 it requires six free fluorine radicals which will then later de-compose back into tungsten onto heated surfaces. The introduction of hydrogen as a reducing gas will form hydrofluoric acid (HF_x). The hazardous nature of chemicals like hydrofluoric acid indirectly helped improve process performance but as it is formed in trace amounts it is unlikely to be a device contamination issue or a safety concern during machine maintenance.

The benefits of H_2 co-gas incorporation [6] can be summarized as follows:

3.1 Stable Source Operation: It has been demonstrated repeatedly in production environments that trace amounts of HF_x produced as a by-product of tying up the F- radicals can chemically etch away the coating on the electrical isolation ceramic insulators so that breakdowns will be minimized and or eliminated. The high chemical volatility of refractory fluorides at ion source operating temperatures has been proven to be detrimental to the arc chamber components. Any gas leakage through and away from the arc chamber tends to coat the insulators between the cathode and arc chamber potential leading to premature failure. Included in the design are patented seals to further minimize the leakage of these corrosive/conductive gases [7]. Best tuning methods and practices must be employed to minimize extraction electrode suppression and ground currents as that is the signature of the beam striking the extraction apertures. The formation of CF_x from the graphite electrode apertures forms a conductive

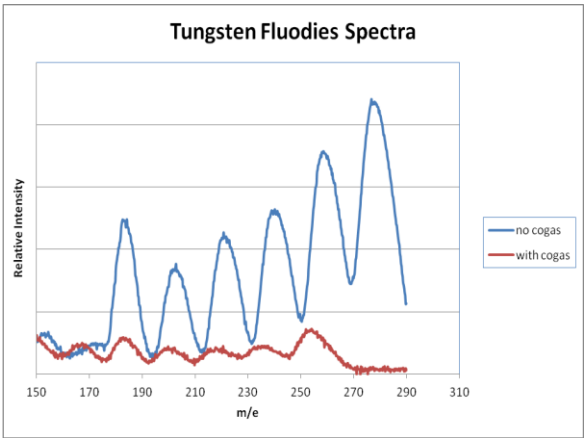

Figure 3: Trace amount of WF_1 (202), WF_2 (221), WF_3 (237), WF_4 (257), and WF_5 (282) can be observed with and without co-gas.

coating onto the high voltage insulators where the micro-discharges occur under high electrical field stress. This discharging which is commonly referred to as glitching has been a problem since the introduction of the ion implant product. The perpetuation of these glitches is further magnified as device nodes shrink as they can be correlated to particles which can increase yield loss and lost productivity through repaints of the wafer. Test A with no H_2 co-gas average number of glitches and high flyers was ~50/hour where Test B with H_2 co-gas was ~1/hour.

3.2 Metal Reductions [8]: When the scattered light reaches a depleted silicon region of an image sensor any defect due to refractory metal contamination shows up as a bright spot. In terms of CMOS image sensors, the production of sensor wafers is similar to those used for devices such as NAND-flash memories and DRAM [9]. During the no co-gas ion source operation, the trace of tungsten chemical compounds: WF_1 (202), WF_2 (221), WF_3 (237), WF_4 (257), and WF_5 (282)

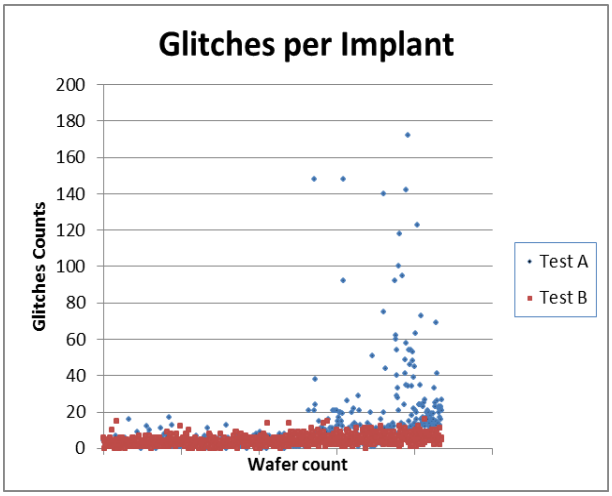

Figure 4: the glitches count over numerous of implants where Test A is the baseline no co-gas and Test B is with co-gas

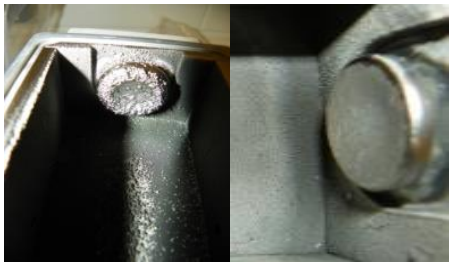

Figure 5: Repeller with and without co-gas after 100 hours of beam operation with and without H_2 co-gas

can be observed, as shown in Figure 3. Even though it can be filtered by the bending magnet it has the tendency to move down the beam line possibly pushed along by the beam or by pressure differentials and it then may deposit onto the wafer as surface contamination. The introduction of the hydrogen reducing co-gas not only stabilizes beam performance (reduced glitching) by the factor of ~50 glitches over hundreds of hours from Test A and B, as shown in Fig. 4 where glitches with co-gas stays fairly stable over a long period of wafer counts. Also, the trace amount of refractory tungsten metal is reduced by a factor of 5 when the co-gas is introduced. Figure 5 Test A shows the interior of arc chamber where the repeller has heavy deposits of tungsten indicating excessive halogen cycle (high formation of WF_6) where Test B with H_2 co-gas shows that the repeller has a slightly eroded surface indication minimal formation of WF_6. Both tests had equal run times with all the same settings except H_2 co-gas.

IV. CONCLUSION

High dose p-type $^{49}BF_2$ and ^{11}Boron can be a productivity challenge for conventional ion implanters used for semiconductor device applications. As device geometries continuously shrink, there is a trend to deliver higher beam currents at lower energies, with a corresponding reduction in particles and metal contamination requirements. From this study, we have demonstrated there are many positive attributes for using H_2 as a co-gas. The results have shown 50 x reductions in glitches for a BF_2 beam throughout source life, reduced W metals contaminant by 5x, and improved ion source lifetimes from 200 hrs to 300 hrs for dedicated BF_2.

REFERENCES

[1] T. J. Hsieh, N. Colvin, S. Kondratenko, Enhanced life ion source for germanium and carbon ion implantation, AIP conf. Proc. 1496, Ion Implantation Technology 2012 372-375 (2012)

[2] Bill Chang and Michael Ameen, *Axcelis Technologies, Inc., Beverly, USA;* "High Mass Molecular Ion Implantation"; http://cdn.intechopen.com/pdfs-wm/17725.pdf

[3] M. Y. L. Jung, R. Gunawan, R. D. Braatz, and E. G. Seebauerz, A Simplified Picture for Transient Enhanced Diffusion of Boron in Silicon, *Journal of The Electrochemical Society*, 151 (2004)

[4] http://www.webelements.com/compounds/tungsten/tungsten_hexafluoride.html; tungsten fluorides Physical properties.

[5] Atsushi et al, "Ion generation device, ion irradiation device, and method of manufacturing a semiconductor device", US Patent 5656820, Aug.12, 1997

[6] Implementation of CO-Gases for Germanium and Boron Ion Implants, US patent 20120119113 A1, Patent Pending.

[7] Special Seals; Patent Pending.

[8] "Implementation reduction of refractory metals contamination on ion implantation", Patent Pending,

[9] Jon Titus, Image-sensor defects can ruin an image, http://www.edn.com/electronics-news/4381021/Image-sensor-defects-can-ruin-an-image, EDN Network, June 01, 2007.