Enriched ¹¹Boron Trifluoride and Hydrogen Mixture for Performance Improvement on Applied Materials E-500 Implanter

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Abstract – A focus of the semiconductor industry on advanced devices and equipment is expected, but many fabs are also at full capacity with legacy node technology. This results in hundreds of older generation ion implanter tools still being used for semiconductor manufacturing processing. The expectation for better yields and lower cost of ownership is always important no matter the technology node. Fluoride gases, including BF₃, have a long history of poor ion source life performance due to tungsten transport from halogen cycling inside the arc chamber. This paper will demonstrate the advantages of mixing only hydrogen (H_2) with enriched ¹¹Boron Trifluoride to increase source life on an Applied Materials (Varian) E-500 ion implant tool. The use of a single subatmospheric cylinder to provide this benefit, makes converting from pure ¹¹Boron Trifluoride to the Entegris ¹¹Boron Trifluoride mixture simple, easy to maintain, and safe.

Keywords — Ion Implant, Dopant, VAC, Boron Trifluoride, BF₃, Hydrogen, H₂, Productivity, Beam Current, Source Life.

INTRODUCTION

Historically, the semiconductor industry has experienced different periods of increased production as well as a reduction in capacity, depending on the end-user product demand. However, one constant throughout this time has been the need for efficiency and optimization of the production tools. In times of high production volume, equipment utilization with maximum process availability is essential. When demand is low other factors may influence key metrics, but to be competitive, manufacturing must still maintain efficient operations.

As the Internet of Things (IOT) continues to expand the use of semiconductor devices, a portion of these devices need leading edge technology to be effective. There is also a segment of the semiconductor market that still can use legacy node devices. Maximizing the equipment performance of legacy implanters through the use of gas mixtures, is the focus of this paper.

Customers of semiconductor devices look for the lowest cost of ownership and best quality, independent of technology node. Entegris' Vacuum Actuated Cylinder (VAC®) Enriched ¹¹Boron Trifluoride (¹¹BF₃) and Hydrogen (H₂) mixture (¹¹BF₃/H₂) has provided source life improvement and lower cost of ownership on current implant tool models.¹ This paper will explore the benefits of using ¹¹BF₃/H₂ on older generation equipment as well.

CONFIGURATION OF OLDER MODEL IMPLANTERS

Control System and Gas Box Compatibility

In these implanter models, software systems use microprocessors mainly for analog and digital selection of the gas dopant and flow rate control. In some cases, software or hard-wired interlocks prevented the gas control system from having any flexibility beyond flowing gas from a single cylinder. This limitation presents an issue as co-flowing multiple gases into the ion source is not possible without significant hardware and software retrofits. These retrofits are not always available on older tools. Therefore, to gain the performance benefits that are enabled with ¹¹BF₃/H₂ mixtures, which will be described later in this paper, it is imperative that the solution be in the form of a precision mixture in a single cylinder. The Entegris ¹¹BF₃/H₂ product which was used to generate the data presented in this paper was a single cylinder containing an optimized mixture concentration for this application.

Along with control system limitations in older generation implanters, previous semiconductor device requirements were limited to the typical primary dopants of arsine, phosphine and boron. The standard gas box allowed four cylinders to be installed. Again, the Entegris ¹¹BF₃/H₂ product is designed to work in older gas boxes, by replacing the single boron cylinder with a single ¹¹BF₃/H₂ mixture cylinder.

For high volume semiconductor manufacturing, the use of co-flow gases to control tungsten transport is critical, though the mechanism by which this control is achieved is complex. To provide optimal beam performance, interactions between primary gas and co-flow gas need to be understood, and precise tuning and adjustments to electrical settings of the arc chamber need to be performed. Ion mass spectrum analysis is required to maximize the desired ion fragments, while minimizing the generation of unwanted ions.³ Legacy implanters do not have the control systems to manage these complex interactions of co-flow gases, or require expensive upgrades if available.

Applied Materials (Varian) E-500 Implanter

The E-500 implanter used in this study was configured as a standard E-500 implanter with Bernas style source and a gas box that holds four cylinders. The results of a comparison of 11BF3 and VAC ${}^{11}\text{BF}_3/\text{H}_2$ mixture demonstrated improved source life and lower cost of ownership using the ${}^{11}\text{BF}_3/\text{H}_2$ mixture.

TUNGSTEN TRANSPORT DUE TO HALOGEN CYCLING

This paper presents the results of improving source life by utilizing a mixture of ¹¹BF₃/H₂, however, it should be noted that ion source performance is similarly improved when employing the same approach on other fluoride dopants, such as GeF₄ and SiF₄. The presence of fluorine in the arc chamber allows fluorine radicals to be created in the ion plasma. These radicals etch the relatively cooler tungsten or molybdenum arc chamber walls or liner and deposit the tungsten or molybdenum on the hotter filament in the ion source.² The transport of the tungsten material from the arc chamber to the filament increases the mass of the filament. When the filament mass increases, the filament power supply cannot sufficiently heat the filament. This limits the generation of electrons needed to sustain the ion source plasma.

The addition of inert gases to enhance cathode sputtering has very little effect on cathode weight change. Just using hydrogen will achieve equivalent cathode weight changes of non-fluorine gases.³ Adding the correct amount of H_2 in the ¹¹BF₃ gas cylinder creates a mixture that provides enough hydrogen to combine with the fluorine radicals thereby reducing tungsten transport, but not stop it completely. This allows some tungsten to deposit on the cathode and replace cathode mass loss during non-fluorine gas operation. The introduction of other gas species in addition to the primary dopant and H_2 may needlessly complicate the gas mixture.⁴

2

Without the 11BF3 /H2 mixture, the metal that deposits on the filament during the tungsten transport mechanism, does not deposit evenly. This results in inconsistent mass across the filament such that there are regions which have additional tungsten and other areas that have eroded tungsten. Providing the correct amount of H_2 to balance the radical fluorine but not contribute to filament erosion is critical to ensuring optimized source life performance.

During the product development phase, highly controlled experiments focused on the effects of tungsten transport were studied. During these experiments, the arc chamber component weight changes were analyzed as a function of the mixture concentration in order to gain insight on the source life performance.⁴ In preparing the mixture for this application, testing was completed to understand the hydrogen concentration which would provide the best performance.²

VAC ¹¹BF₃/H₂ QUALIFICATION PLAN

With all process material changes, process qualification testing is required to ensure there is no unintended impact to device parameters. In the testing presented in the following sections, the qualification plan included verifying beam spectrum, sheet resistance, source lifetime and comparing the results with VAC ${}^{11}\text{BF}_{7}/\text{H}_{2}$ to Entegris' SDS[®]3 ${}^{11}\text{BF}_{7}$.

The initial qualification test was to run an Atomic Mass Spectrum (AMU) scan to verify that there were no unexpected changes with ${}^{11}\text{BF}_3/\text{H}_2$; the results are shown in Fig 1. The process team's analysis confirmed that the standard ${}^{11}\text{BF}_3/\text{H}_2$ recipe showed only expected isotopes. Hydrogen, which is an active component of the mixture, was almost undetectable.

The next qualification step was to check Sheet Resistance (Rs). Several months of baseline Rs data was compared to test results after installing ${}^{11}\text{BF}_3/\text{H}_2$. The vertical line by sample 17 in Figure 2 identifies the point in time where the ${}^{11}\text{BF}_3/\text{H}_2$ cylinder was installed. The outlier values have been identified by comment boxes with an assignable cause not related to ${}^{11}\text{BF}_3/\text{H}_2$. Analysis by the process team found no significant change to sheet resistance after the introduction of ${}^{11}\text{BF}_3/\text{H}_2$.

¹¹BF₃/H₂ RESULTS

Key performance metrics for ion implantation include many process aspects which ${}^{11}\text{BF}_3/\text{H}_2$ successfully passed. The equipment related parameters are the focus of this report.

Beam current performance can affect equipment throughput, and impact process module cycle time. A comparison of the beam current data over time suggest no change in beam performance as shown in Fig 3. The vertical line on sample 16 is the date the material supply changed from 11BF3 to ¹¹BF₃/H₂. The use of a two-sample t-test to compare the ¹¹BF₃ mean beam current and the ¹¹BF₃/H₂ mean beam current, revealed the two means were not significantly different (p=0.774).

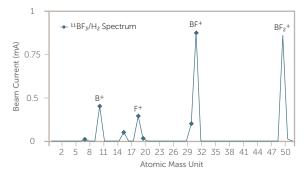


Figure 1. AMU spectrum

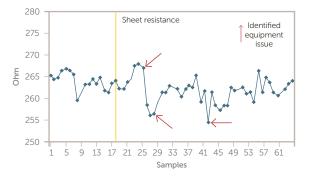


Figure 2. Sheet resistance

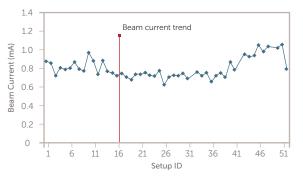


Figure 3. Beam current trend

A key maintenance parameter to measure equipment performance is tool availability, and one of the major drivers that impacts the total time an ion implant tool is available for production is the ion source lifetime. Reducing tungsten transport not only reduces the deposits on the filament or cathode, but also reduces the arc and electrode slit erosion. Reducing the metal transport in the arc chamber reduces the metal available to plate insulators which is a source of glitching. Electrode wear can affect beam optics and in some implanters, create beam uniformity errors.

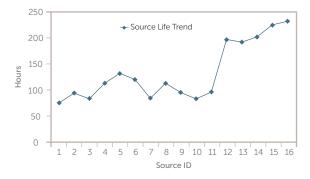


Figure 4. Source life trend

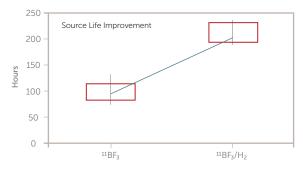


Figure 5. Box plot of source life improvement

The demonstration of source life improvement is shown in Figure 4. The source life graph details an average source life of 99 hours with ${}^{11}\text{BF}_3$. Once the ${}^{11}\text{BF}_3/\text{H}_2$ mixture was introduced the average source life increased 111% to 209 hours as seen in Figure 5. Reducing source changes by 50% and increasing reported tool uptime 1.7% allowed for more efficient use of technician time in maintaining the Implant module. Increasing uptime also provided additional time to process wafers reducing module cycle time.

Cylinder change out frequency was not calculated in the cost of ownership improvement during this evaluation. For customers that use SDS3 ¹¹BF₃ and need to consider benefits found in Entegris mixtures, increased gas deliverables come with the VAC ¹¹BF₃/ H₂. The JY SDS3 ¹¹BF₃ cylinder delivers 330 grams of gas down to a cylinder pressure of 5 torr. The VAC ¹¹BF₃/H₂ contains 525 grams of ¹¹BF₃. VAC ¹¹BF₃/H₂ provides 59% more gas over SDS3. No major change to gas flow was reported when moving from ¹¹BF₃ to ¹¹BF₃/H₂ and a simple calculation based on product deliverables indicates ¹¹BF₃/H₂ cylinder will last 59% longer in the implanter than SDS3 ¹¹BF₃. If needed, a larger cylinder package can provide 1,650 grams of ¹¹BF₃/H₂. This larger package allows for increased cylinder life and reduced cylinder changes. Utilizing the largest cylinder package the implanter will accept, not only reduces maintenance time but reduces risk associated with cylinder changes, and typically provides a lower cost per gram of gas.

Another key metric is the cost of running the implanter or Cost of Ownership (COO). Cost of Ownership is important in all aspects of equipment productivity. The use of poor quality consumables can directly affect equipment productivity. This includes gas cylinder packages. Cylinder packages that have repeated failures have a higher COO even if the price of the cylinder is lower. This can be extended to the gas in the cylinder as well. If the gas in the cylinder has a known negative effect on the source and moving to a higher quality gas removes the negative effect, the overall benefit can improve COO. Utilizing ${}^{11}\text{BF}_{z}/\text{H}_{2}$ doubles the mean source life of the E-500 implanter. This cut the cost of source rebuilds in half. Rebuilding less sources also reduces labor cost for the source rebuilding process.

As an example of the potential cost of ownership benefit when switching to a product such as ${}^{11}\text{BF}_3/\text{H}_2$ which provides productivity improvements, first consider the cost of a source rebuild. For this example, a single source rebuild cost of \$2,500 is estimated. A source that is used for 100 hours equals an hourly cost of \$25. This does not include the cost of downtime to replace the source from lost productivity, and technical resources. Depending on post source replacement qualification time, an implanter can be out of production for 3 to 6 hours or more for a source change. This lost production time can easily contribute to thousands of dollars wasted. Even when excluding these costs, a doubling in source life results in an hourly cost savings of \$12.50.

Depending on process recipes, the hourly cost of the gas species may roughly range from 5-10/hr. So in effect, utilizing the ¹¹BF₃/H₂ mixture provides savings in this example in excess of the total gas cost itself.

In line with this example, utilizing the ${}^{11}\text{BF}_3/\text{H}_2$ mixture saves thousands of dollars by doubling source life, which cuts source rebuild cost in half. Reducing source changes from six a month to three a month provides increased uptime and module production capacity, lowering module cycle time. These savings cut monthly Implant expense, and ultimately reduce the cost per wafer. During the evaluation on the E-500 the COO benefit was positive providing a Return on Investment (ROI) that justified making the ${}^{11}\text{BF}_3/\text{H}_2$ solution the Process of Record.

BF₃ MIXTURE SELECTION

Ion Implanter designs have changed over the years as both the use increased in the early 1980's as well as technology needs changed which required advancements in equipment design. However, as ion implanter OEMs designed new tools for changing application needs, there still has been a relatively large segment of the older install base of implanters that are still in use. The implanter models developed in the 1990 and 2000's can provide value for select users. Certainly, a majority of the installed implanter base is from implanter models from mid-2000 until now.

Depending on the dopant dose and depth requirements three basic models service most of the semiconductor needs. These are medium current implanters that provide mid energy to high energy acceleration voltages, high current implanters that provide low energy to mid energy range and high energy implanters that provide megavolt energy levels. The use of boron dopants varies as a percentage of total dopants implanted based on the respective implant step. Implant steps are grouped within the three basic model implanters and this can change the boron dopant mix that some implanters process.

Another variant that impacts implanter use is the wide range of semiconductor device designs. Over the years consolidation of semiconductor manufacturers have merged design rules but each fab can have its unique approach to device requirements. This may influence the percent of boron a customer utilizes compared to hydride gases. Production run rules for balancing hydride verse fluoride dopants may also play a factor in optimizing source performance.

It is understood that one mixture may not suit all model implanters or all customer process needs. For this reason, Entegris offers more than one mixture to allow for a simple single cylinder solution that is tailored to customer needs. Supplying the ideal mixture ratio in a single cylinder not only offers simplicity in use, but it also removes the risk of a separate hydrogen cylinder and the risk associated with using two cylinders to accomplish the same benefit as a single VAC cylinder.

The ${}^{11}\text{BF}_3/\text{H}_2$ mixture gas is offered in the VAC package, which is a Subatmospheric Gas Source (SAGS) Type II gas delivery system. Incorporating only specially designed components, the cylinder stores the gas mixture at a pressure greater than 500 psig, but delivers the mixture at a pressure of less than 14.7 psia.

The chemical stability of BF3 and H2 in this mixture is one of the most important safety and functional characteristics of this product. Thermodynamic calculations show that no reaction occurs between BF3 and H2 at room or elevated temperatures as exemplified by the reaction equation below (as well as others that can be contemplated):¹

 $BF_3(g) + 1.5H_2(g) = B(s) + 3HF(g) \Delta_r G^{25 \circ C} = 293 \text{ kJ}^1$

Lack of reactivity is shown by the positive Gibbs energy of reaction, indicating the reactants (i.e. the mixture components) are highly favored thermodynamically over any products. ⁴ The stability of the mixture enables a 3-year shelf-life.

SUMMARY

As process controls increase to minimize process variation, the use of a premixed process gas removes one source of implanter setup variation. This has the added benefit of less engineering intervention to maintain optimum implanter efficiency. The VAC ¹¹BF₃/H₂ mixture allows customers to select the best mixture concentration for their specific process environment, with a package that is simple to install. The VAC cylinder uses quality designed components to provide subatmospheric gas pressure delivery for any common gas box design. The VAC package easily can replace the existing BF₃ cylinder allowing the benefits of hydrogen to inhibit the halogen cycle created by fluorine based gases.

Semiconductor manufacturing sites that have many years of service need to use best practices to stay competitive. From the information provided in this paper the use of the VAC ¹¹BF₃/H₂ mixture has demonstrated a doubling of source life in an implanter model (E500). This resulted in more wafer turns due to increased availability, lower manufacturing cost per wafer based on extended use of source parts, and better implanter availability. Semiconductor device demand is increasing, device nodes change over time, but the implant process remains relatively constant. The energy, dose, or species mix may vary but older implanters are still effective and the use of additional dopant mixtures to improve equipment performance is important to consider.

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