

A Vaporizer for Decaborane and Octadecaborane

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Abstract. Decaborane ($B_{10}H_{14}$) and Octadecaborane ($B_{18}H_{22}$) are two promising new doping materials for performing very shallow boron implants at high implanter throughput. However, because these new materials are low-vapor pressure solids at room temperature, their delivery to the implanter's ion source requires specialized techniques to deliver the desired mass flow without condensation. Data are presented which describe several features of a vaporizer for producing Decaborane and Octadecaborane flows in a production environment. This paper will also focus on the critical design aspects of the vapor delivery system, including the effects of vaporizer geometry on vapor flow rate, the performance of various flow control systems, and the overall thermal design. In addition, data on physical and environmental, safety, and health properties of these materials are presented. The effectiveness of this system as a stable vapor source for an ion implanter will be described.

Keywords: Decaborane, Octadecaborane, ClusterBoron[®], Vaporizer, Ion Source.

INTRODUCTION

Ion implantation utilizing borohydride molecules such as decaborane and octadecaborane allows for the extraction and transport of ion beams at much higher energies. These implant materials offer a solution to the problems of throughput and energy contamination.

The use of these feed materials for ion sources have introduced several technical challenges that must be practicably overcome in order to safely and effectively deliver these materials into an implanter for the manufacturing of semiconductor devices.

In order to use decaborane and octadecaborane in implanters, the system must be able to deliver toxic material in vapor form to an ionization source located in a high vacuum system. These materials are solids and have low vapor pressure at room temperature. The vapor stream must be accurately controlled in order to achieve a stable and consistent flow of molecules to the ionization chamber. Reliably controlling these vapor streams requires heating the solid material in order to increase the rate of sublimation and therefore the vapor pressure.

Raising the temperature of borohydrides entails certain safety hazards. These hazards are toxicity, chemical decomposition and chemical reaction of the vapors if brought in contact with certain substances.

For a production implanter, the consumption of solid materials requires their periodic refill. This routine maintenance requires the correct sequence of breaking and making vacuum seals, system re-qualification, and special handling and service procedures to ensure personnel safety.

A comprehensive understanding of the characteristics of these materials, and the incorporation of this understanding into the equipment design, results in a safe and effective vapor delivery system.

VAPOR PRESSURE & THERMAL SENSITIVITY

Solid borohydrides have relatively low vapor pressures at room temperature. Figure 1 shows vapor pressure for decaborane and octadecaborane. These materials have relatively low vapor pressures when compared to conventional implant gases such as those delivered in high pressure gas bottles or SDS[™] bottles. The low pressure prevents the application of conventional Mass Flow Controllers (MFC's) for vapor regulation. Raising the temperature in order to increase pressure is limited due to chemical decomposition of the borohydride compounds. Safety considerations also become a factor at elevated temperatures. It is possible that a sudden exposure to

air at elevated temperatures can result in ignition of the material.

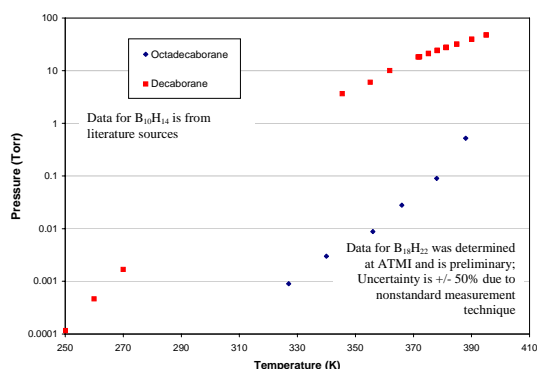


FIGURE 1. Vapor Pressure of decaborane [1,2] and octadecaborane.

Both decaborane and octadecaborane must be heated in order to achieve the pressure (>100mTorr) necessary for vapor transport to an ionization chamber. A pressure difference and a simple means of adjusting the conductance between the vapor source and the ionization chamber must exist in order to regulate the vapor mass flow rate. Heating of the borohydrides must be controlled with sufficient heat transfer surface area (conduction and radiation) to provide an adequate rate of sublimation. Providing excessive heating or heating too quickly may lead to disassociation of the molecules. Perel *et al* report [3] that rapid decomposition of decaborane [1] above 350°C can be readily observed, as indicated in Figure 2. Below 300°C, hydrogen partial pressure is much lower,

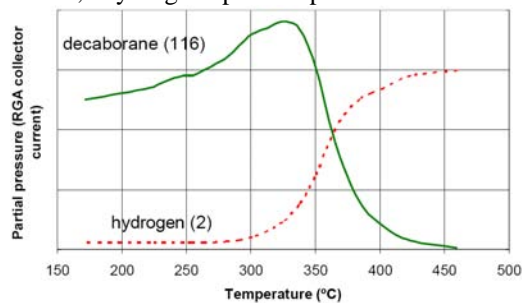


FIGURE 2. Partial pressure of Decaborane and Hydrogen while heating Decaboane until complete decomposition

indicating a very low rate of disassociation. Initial studies by ATMI into the decomposition of octadecaborane is represented in Figure 3. An experiment was conducted wherein the total vapor pressure of a heated sample was observed over time at five different temperatures. As temperature was increased, the rate of pressure rise appeared to increase. This is thought to be due to the buildup of hydrogen disassociated from octadecaborone, much as seen by Perel *et al* [3] for decaborane.

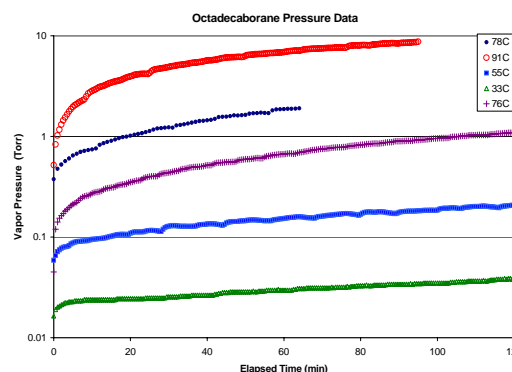


FIGURE 3. Measured vapor pressure of octadecaborane over time at various temperatures.

SUBLIMATION AND CONDENSATION

The solid borohydrides must be heated in order to create sufficient vapor pressure for transport to the source ionization chamber, where the pressure is maintained in the milliTorr range, and the region immediately outside of the ion source is at high vacuum. The gas vapors must be transported at temperatures below the melting point' however, sufficiently high temperature must be maintained to prevent condensation of the vapor. Condensation occurring between the vaporizer and the point of ionization can lead to transport failure. When the vapor path becomes partially occluded, this results in wasted source materials, poor vapor flow control, and beam instabilities that lead to degraded Implanter productivity. The vaporizer and vapor transport system were designed to thermally manage the temperature of the wetted surfaces, as shown in Figure 4.

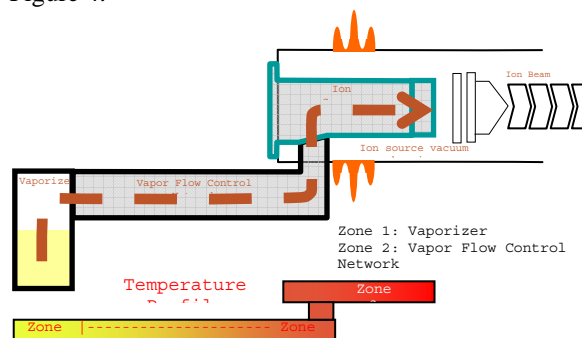


FIGURE 4. Vapor flow path from vaporizer to source ionization chamber

As the vapor travels from its point of sublimation, the walls along the vapor path are at increasingly higher temperature until reaching the ionization chamber. This is accomplished by managing three loosely coupled thermal zones and the effective distribution of

heat sources. Aluminum is used for vapor passages and thermal insulation is used to maximize thermal uniformity.

THE VAPORIZER

The vaporizer consists of a two-piece factory refillable canister and isolation valve, shown in Figure 5. The bottom section provides the heat transfer surfaces necessary to sublimate the solid materials.

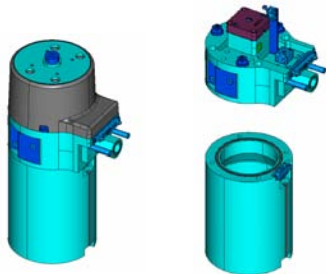


FIGURE 5. Commercial borohydride vaporizer shown with valve and heating head separated.

A temperature sensor is located in the lower section to provide temperature feedback to a closed loop PID controller. The top serves several functions: Closure to the canister, location for a vapor isolation valve, mounting position for heating elements, and thermal mass for distributing thermal energy to lower section.

This design achieves a positive thermal gradient from the bottom to the top, as indicated in Figure 6. The advantage is improved serviceability to the vaporizer isolation valve and control of condensing vapors. The upper section remains warmer than the

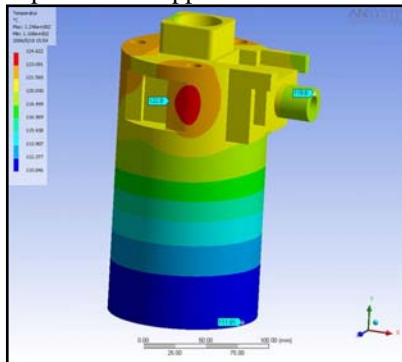


FIGURE 6. Thermal analysis of commercial borohydride vaporizer.

lower section. Gas vapors are most likely to condense back onto the lower section (coolest region) of the vaporizer thereby eliminating solid buildup on moving surfaces (*i.e.* valve). Additionally, a consumed vaporizer is unlikely to have any residual solid material remaining in the vapor path.

For production implanters, rapid recovery following a shutdown is important. The vaporizer

must contain sufficient thermal heat transfer surfaces (primarily aluminum) and thermal energy to enable a thirty minute recovery from room temperature, see Figure 7. The surfaces in contact with the solid material being vaporized are located away from the heating elements. This heater location provides for a thermal gradient between the vaporizer exit and the bottom of the vaporizer. During heating, less than a 10°C variation exists between the vapor exit and bottom of the vaporizer.

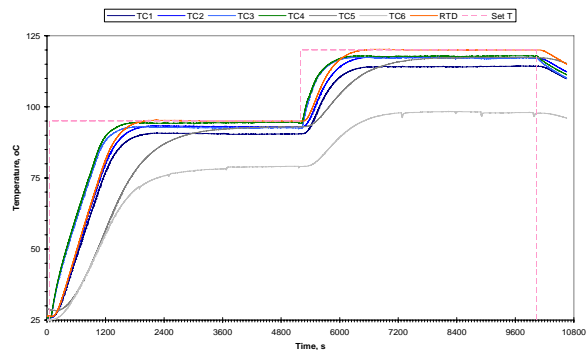


FIGURE 7. Thermal ramp of instrumented vaporizer, 25°C to 95°C hold one hour; 95°C to 120°C hold for one hour

This allows for sufficient thermal power to be added to the vaporizer for rapid heat up without the risk of disassociation of the vaporized material.

VAPOR FLOW CONTROL

An Implanter source must have a carefully regulated supply of feed gas in order to provide a stable ion beam. Conventional ion sources use MFC's for this function. MFC's are not able to regulate gas flows for octadecaborane and decaborane due to their requirement for a relatively high inlet pressure and pressure drop across the MFC. Figure 8 provides an example of a valve network that provided regulated molecular flow of gas vapor to an ion source.

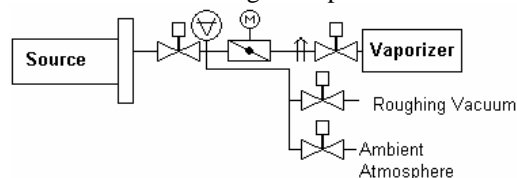


FIGURE 8. Vaporizer to source flow diagram.

The system consists of a vaporizer device capable of sublimating solids at a sufficient rate to provide a positive pressure across a conductance throttling device, and a vaporizer isolation valve to provide positive shut off of vapors from the vaporizer. A variable conductance is achieved using a commercial available servo-actuated vacuum butterfly valve

controlled with a PID controller. Feedback control to the servo controller comes from a downstream heated pressure transducer. Other valves are shown that aid in vacuum pump down and venting for service.

The conductance between the throttle valve and the ionization source is fixed. The pressure of the vaporizer will change with vaporizer temperature setting, and is based on the amount of solid material available in the vaporizer canister. As the solid material depletes, the vapor pressure in the vaporizer drops due to a reduced mass rate of vaporization, since the volume and surface area of the solid material is reduced as the material is consumed. In addition, the heat transfer flux (in W/cm^2) is proportional to the temperature of the vaporizer. This results in reduced thermal energy being absorbed into the solid; thus, if the temperature is left constant, the rate of sublimation and also the inlet pressure to the servo valve diminishes as the solid material is consumed. The servo valve will open further to compensate for the lower inlet pressure. Over time, it is therefore necessary to raise the temperature of the vaporizer to compensate for the reduced sublimation rate. Since the mass flow of vapor into the ion source directly influences the ionization rate in the source, maintaining a stable flow necessary to produce a stable beam current.

Figure 9 shows the transient system response

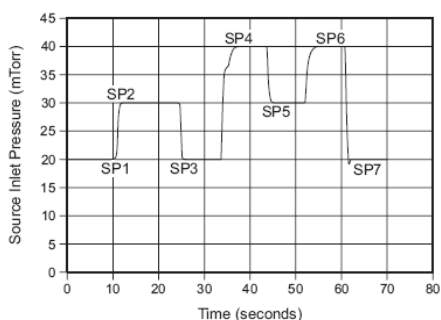


FIGURE 9. Flow control system response to step changes in control setpoint. SP1—SP7 refer to pressure set points.

of the valve controller when subjected to a series of 50% and a 100% changes in pressure (proportional to mass flow) set points. The valve controller was able to compensate for in flow setting. Since changes to pressure set point typically occur during beam tuning events, rapid system response is critical in order to quickly achieved desired ion beam properties.

VAPOR SOURCE SERVICING

Conventional implant gases are distributed in gas bottles. The technology used may be conventional high pressure gas cylinders, or more advanced technology such as SDS or VAC gas cylinders. These

devices are engineered to meet safety regulations assigned by industry and international commerce. Due to the characteristics of decaborane and octadecaborane, none of these existing distribution techniques are applicable. The concept of a replaceable bottle was chosen so as to remain consistent with current service techniques and periodicity. A distribution container that can also serve as a point of vaporization would have many advantages. The container is directly mounted to the vapor delivery system of Figure 8. In order to eliminate operator exposure and other potential hazards, a combination of hardware features were designed into the container and container mounting interface:

Potentially Hazardous Conditions:

- Toxic vapors emitted from the container
- Exposing oxygen to solid borohydride compounds at highly elevated temperatures
- Heated surface may cause burns to the skin

Safety Design Features:

- The vaporizer is mechanically interlocked from being removed unless the isolation valve is locked shut
- The vaporizer isolation valve is mechanically locked shut unless the vaporizer is properly secured to the vaporizer mount
- All readily accessible heated surfaces are thermally insulated to protected service personnel

CONCLUSION

We have developed a vaporizer system for decaborane and octadecaborane. The vaporizer is capable of delivering the performance and reliability required by commercial ion source systems. The vaporizer has been tested on several SemEquip, Inc. ClusterIon[®] source systems and on a GSD/100 implanter that has been retrofitted with ClusterIon[®] source technology.

A means for safe delivery and integration of Borohydride materials into an implanter has been shown. This development effort further enables the use of decaborane and octadecaborane doping materials for performing very shallow boron implants at high implanter throughputs.

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