APPLICATION NOTES: PROCESS GUIDELINES FOR USING BORON TRIBROMIDE (BBr₃)

DESCRIPTION
Boron tribromide (BBr₃) is a liquid boron source used for creating P-Type regions in silicon substrates. Dopant levels can be easily controlled by adjusting the deposition and diffusion processes. Typical applications include base and isolation regions in bipolar devices and source, drain and isolation regions in MOSFET devices.

PHYSICAL CHARACTERISTICS

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>BBr₃</td>
</tr>
<tr>
<td>Liquid Density</td>
<td>2.67 g/ml at 20°C</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>250.54</td>
</tr>
<tr>
<td>Relative Density</td>
<td>8.65 (air=1)</td>
</tr>
<tr>
<td>Flash Point</td>
<td>Nonflammable</td>
</tr>
<tr>
<td>TLV</td>
<td>1 ppm</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>91.3°C at 1 atm</td>
</tr>
<tr>
<td>Freezing Point</td>
<td>-46°C</td>
</tr>
</tbody>
</table>

CHEMISTRY
BBr₃ oxidizes at process temperatures with oxygen to form B₂O₃. This in turn reacts at the silicon surface to form elemental boron and silicon dioxide, as follows:

\[ 4\text{BBr}_3 + 3\text{O}_2 \rightarrow 2\text{B}_2\text{O}_3 + 6\text{Br}_2 \]
\[ 2\text{B}_2\text{O}_3 + 3\text{Si} \rightarrow 4\text{B} + 3\text{SiO}_2 \]

PROCESS CONTROL
The amount of dopant introduced into the diffusion tube depends on the bubbler temperature, the nitrogen carrier flow rate and the pressure of the process. The most common bubbler temperature used for this type of application is 21°C. The bubbler temperature is generally stabilized using a temperature controller and is set at least 5°C below the temperature of the process lines connecting the bubbler to the furnace in order to prevent condensation. The nitrogen flow rate is usually controlled using a mass flow controller as accurate and repeatable gas flow is required. The pressure of most systems is dictated by the atmospheric pressure; therefore, the atmospheric pressure should be taken into consideration when calculating the product flows.
The starting point for setting source process conditions is the vapor pressure. The vapor pressure curve for BBr₃ is displayed in Figure 1.

**Fig. 1—Vapor Pressure Curve for BBr₃**

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**CARRIER GAS**

High-purity nitrogen is the most frequently used carrier for BBr₃ and highly recommended although other inert carrier gases can be used. The moisture specification for the carrier must be within the range of 10-50 ppb. The moisture specification is very important as BBr₃ reacts violently with moisture to form boric acid and hydrogen bromide. Caution: Only inert gases should be used as carriers, oxygen should never be used as a carrier gas for BBr₃ applications.

\[ \text{BBr}_3 + 3 \text{H}_2\text{O} \rightarrow \text{B(OH)}_3 + 3 \text{HBr} \]

**COMPATIBILITY**

BBr₃ is corrosive to most metals and is water sensitive which further enhances its corrosivity through the formation of hydrogen bromide.

The recommended material of construction for process lines is Teflon® Perfluoroalkoxy (PFA). This material is relatively transparent and malleable, and resistant to acids and temperatures in excess of 200°C.

**CHEMICAL MASS FLOW RATES**

The mass transfer, or pick-up rate, equation defining systems running at local atmospheric pressure is defined as:

\[
M_{\text{BBr}_3} = \frac{P_{\text{vap}}}{P_{\text{local}} - P_{\text{vap}}} \times Q_{\text{N}_2} \times \left[ \frac{\text{MW}_{\text{BBr}_3}}{22414} \right]
\]

Where:

- \( M_{\text{BBr}_3} \) = BBr₃ Pickup Rate in grams per minute.
- \( P_{\text{vap}} \) = BBr₃ Vapor Pressure (Torr) at bubbler temperature.
- \( P_{\text{local}} \) = Atmospheric pressure in Torr.
- \( \text{MW}_{\text{BBr}_3} \) = Molecular weight of BBr₃.
- \( Q_{\text{N}_2} \) = Flow of the high-purity nitrogen carrier gas in sccm.
The following example calculates the BBr$_3$ pickup rate at various temperatures and various nitrogen flow rates at 760 Torr (1 atmosphere, sea level)

<table>
<thead>
<tr>
<th>N$_2$ Flow (sccm)</th>
<th>15°C</th>
<th>20°C</th>
<th>30°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>50</td>
<td>0.032</td>
<td>0.040</td>
<td>0.067</td>
</tr>
<tr>
<td>75</td>
<td>0.047</td>
<td>0.060</td>
<td>0.100</td>
</tr>
<tr>
<td>100</td>
<td>0.063</td>
<td>0.080</td>
<td>0.134</td>
</tr>
<tr>
<td>150</td>
<td>0.095</td>
<td>0.120</td>
<td>0.200</td>
</tr>
<tr>
<td>200</td>
<td>0.126</td>
<td>0.160</td>
<td>0.267</td>
</tr>
<tr>
<td>300</td>
<td>0.189</td>
<td>0.240</td>
<td>0.401</td>
</tr>
<tr>
<td>350</td>
<td>0.221</td>
<td>0.280</td>
<td>0.468</td>
</tr>
</tbody>
</table>

These results are geographically represented in the following:

**SETTING UP THE PROCESS**

The information presented below is general in nature and meant to produce a working set of oxidation conditions. These conditions can be further refined to develop a process that will be unique to a set of process specifications. Therefore, this information, as presented, although representative, provides a starting point and not a final process condition.

Figure 4 represents a simplified schematic of a typical process and should be referred to in the following steps.

1. Calculate the volume of the process tube using the formula below:

$$V_t = \frac{\pi \times L \times r^2}{1000}$$
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\[
V_t = \frac{\pi \times L \times r^2}{1000}
\]

Where:
- \(V_t\) = total volume of the tube in liters
- \(L\) = length of the tube in centimeters
- \(r\) = inner radius of the tube in centimeters

2. The exchange rate (ER) is defined as the number of gas exchanges within the process tube per unit time. This ensures an adequate supply of product to the wafer surface. The ER is generally dictated by the process parameters but is typically one exchange every 5 to 10 minutes. This is the exchange rate time.

3. The main gas flow rate can be calculated by dividing the volume of the process tube by the exchange rate time. For example, if the volume of the process tube is 40 liters and an exchange rate time of 8 minutes was chosen, then the main carrier gas flow rate will be 5 L/min.

4. Calculate the flow of oxygen needed for the oxidation step. It is usually 5% of the main gas flow. In the example in Step 3, the oxygen flow rate will be 5% of 5 L/min or 0.25 L/min oxygen.

5. Next is to determine the flow rate of the carrier gas. The carrier gas flow and bubbler temperature are the main variables that determine the amount of BBr3 delivered to the furnace. As the carrier gas bubbles through the liquid it "picks up" BBr3 and delivers it downstream. The pick-up rate is the amount of BBr3 delivered per unit time and can be determined from the oxygen flow. Oxygen must be in excess as compared to the BBr3 to ensure full oxidation. The molar ratio is generally in the range of 30:1 \(\text{O}_2\) to BBr3. In the example above, 0.25 L/min \(\text{O}_2\) is equivalent to 0.011 moles of \(\text{O}_2\) per minute on an ideal basis (0.25 L/min / 22.4 L/mole). The molar BBr3 pick-up rate should be approximately 0.00037 mole/min or 0.94 gram/min. The table below was derived from the data in Figures 2 and 3 and represents the impact of the bubbler temperature on the carrier flow rate for the calculated pick-up rate.

<table>
<thead>
<tr>
<th>(Q_{\text{O}_2}) (SCCM)</th>
<th>(M_{\text{BBr3}}) (gram/min)</th>
<th>Bubbler Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>148.99</td>
<td>0.094</td>
<td>15°C</td>
</tr>
<tr>
<td>117.54</td>
<td>0.094</td>
<td>20°C</td>
</tr>
<tr>
<td>70.35</td>
<td>0.094</td>
<td>30°C</td>
</tr>
</tbody>
</table>

Fig. 5—Calculation of flow for a given pick-up rate, at various temperatures

Equation 1 found on Page 3 can be used to calculate the effect of atmospheric pressure on the carrier gas/BBr3 flow rate.

\[
M_{\text{BBr3}} = \left[\frac{P_{\text{vap}}}{P_{\text{local}} - P_{\text{vap}}}\right] \times Q_{\text{N}_2} \times \left[\frac{\text{MW}_{\text{BBr3}}}{\text{MW}_{\text{N}_2}}\right]
\]

Eq. 1

The equation is generally used when a constant pick-up rate (\(M_{\text{BBr3}}\)) is desired at a specific temperature which directly corresponds to a specific vapor pressure (pvap) and a change in atmospheric pressure (plocal). Rearranging the equation for a specific temperature, i.e. vapor pressure, yields:

\[
\frac{M_{\text{BBr3}} \times \text{MW}_{\text{BBr3}}}{P_{\text{vap}} \times \text{MW}_{\text{N}_2}} = \frac{Q_{\text{N}_2}}{P_{\text{local}} - P_{\text{vap}}} = \text{Constant}
\]

Eq. 2

And further arrangements yields:

\[
Q_{\text{N}_2} = \text{Constant} \times (P_{\text{local}} - P_{\text{vap}})
\]

Eq. 3

Where:
- \(Q_{\text{N}_2}\) = the flow of the high-purity nitrogen carrier gas in sccm
- \(P_{\text{vap}}\) = the vapor pressure of BBr3, at bubbler temperature, in Torr
- \(P_{\text{local}}\) = the atmospheric pressure in Torr
Using atmosphere pressure, 760 torr, as the initial calculated condition:

\[ Q_{N2initial} = \text{Constant} \times (760 - P_{vap}) \quad \text{Eq. 4} \]

A ratio can now define the correction for pressures other than atmospheric pressure in terms of a percentage of the original calculated flow:

\[ F = \left[ 1 - \frac{Q_{N2}}{Q_{N2initial}} \right] \times 100 \quad \text{Eq. 5} \]

F is the percent flow correction. For atmospheric pressures less than 760 torr, the flow will be reduced by this percentage and for pressures greater than 760 torr, the flow will be increased by this percentage.

Using the example in previous steps, Figure 6 shows the flow corrections for various temperatures.

<table>
<thead>
<tr>
<th>Atmospheric Pressure (torr)</th>
<th>Percent Flow Correction</th>
</tr>
</thead>
<tbody>
<tr>
<td>680</td>
<td>15°C 20°C 30°C</td>
</tr>
<tr>
<td>720</td>
<td>5.5 5.6 5.9</td>
</tr>
<tr>
<td>760</td>
<td>0.0 0.0 0.0</td>
</tr>
<tr>
<td>800</td>
<td>-5.5 -5.6 -5.9</td>
</tr>
</tbody>
</table>

**Typical Furnace Process Sequence**

* The purge cycle is to ensure that an oxidizing atmosphere remains in the tube until all of the BBr3 reaches the exhaust. The time for this step should be no shorter than the exchange rate.
GENERAL PROCESS AND SAFETY NOTES

General Process and Safety Notes

- For purging and cleaning the downstream lines of the bubbler use a by-pass system as shown in Figure 4.
- Avoid three-way and check valves in the process lines from the bubbler to the process tube as they are prone to clogging in BBr₃ service.
- Ensure that the process lines downstream of the bubbler are kept at least 5°C warmer than the product temperature. This is to prevent condensation of the product in the process lines.
- Oxygen is never to be mixed with the BBr₃ prior to entering the furnace. Nitrogen / BBr₃ and Nitrogen / Oxygen gas streams are introduced into the furnace separately (see Figure 4). The mixing zone is typically heated to 870°C thus allowing for oxidation. The gas streams are diffused to the deposition zone at a typical temperature of 910°C.
- During the process run, white crystals of H₃BO₃ and/or a clear to brown liquid primarily composed of HBr may form downstream of the process tube. These are formed through condensation of the reaction product and can be minimized or avoided by reducing the process flow or through proper heating of the exhaust line in order to eliminate any cooler sections of the line.

Safety and Handling of BBr₃ Bubblers

- The materials of construction of the typical bubbler (See Figure 7) are quartz glass for the body, valve tubing, diptube and thermowell. The valves are a corrosion resistant perfluoroelastomer.
- The body of the bubbler is coated to protect against breakage and provide extra stability; however, bubblers must not be exposed to pressures in excess of 15 psig. Use Pressure Relief Valves (PRV) on the carrier line upstream of the bubbler that are set at 15 psig or lower (see Figure 4).
- When opening the bubbler valves be sure that the body of the valve is supported to prevent the valve from twisting on the bubbler tubing.
- Remove the shipping plugs from the outlet of both valves by disconnecting the outlet hex nut then removing the plug and reconnecting the hex nut.
- BBr₃ bubblers are shipped under negative pressure and should be opened only after connection to a purged system to prevent back-flow of air into the system.
- The ¼” inlet valve of the bubbler is equipped with a dip tube that extends into the liquid phase, the ⅜” outlet valve extends only into the vapor phase of the bubbler.
  - Both the inlet and the outlet valves are internally sealed with a thin quartz diaphragm that must be broken before use by closing each valve.
  - When opening the bubbler, never open the inlet valve before opening the outlet valve as the differential pressures within the bubbler and carrier lines may cause the product to be siphoned back into the carrier line.
  - When closing the bubbler, always close the inlet valve before the outlet valve.
BBr₃ Accidental Release

- Evacuate personnel to a safe, uncontaminated area
- In the event of an emergency, contact supplier for guidance using the Emergency Telephone Number listed in the MSDS
- When responding to an accidental release, use self-contained breathing apparatus, suitable chemically protective clothing, chemical resistant gloves and eye/face protection.
- Approach suspected leak areas with caution as the fumes from the leaking product are corrosive.
- If possible, stop the flow at the source and construct a dike to prevent the spread of liquid.
- Use an inert absorbent material such as vermiculite directly on the spill and let stand until all the liquid is absorbed. Note that fuming of the product should be reduced but may not fully subside.
- Keep the spill area protected from water and ventilate to the outside if possible.
- Place the used vermiculite in an appropriate chemical waste container.
- Contact your Safety Department for information on proper disposal.

The information given is provided to furnish starting points for the process engineer. The final determination of gas flows is individual and is unique with each furnace installation.