APPLICATION NOTES: PROCESS GUIDELINES FOR USING PHOSPHOROUS OXYCHLORIDE AS AN N-TYPE SILICON DOPANT

DESCRIPTION
Phosphorus Oxychloride (POCl₃) is a liquid Phosphorus source used for diffusion of N-type regions into silicon substrates. The dopant levels may be controlled to provide near solid solubility levels for use in bipolar devices or lighter doped regions in MOS devices. The dopant material can be used to form emitter areas for bipolar devices, source/drain and doped polysilicon applications for MOS device structures.

CHEMISTRY
Phosphorus Oxychloride (POCl₃) oxidizes at normal process temperatures with oxygen to form P₂O₅. This material is reduced by reaction with the silicon exposed at the surface of the wafer to form elemental phosphorous and silicon dioxide. At this point the phosphorus diffuses into the silicon at a rate determined by the temperature of the furnace. Diffusion depth or junction depth, (Xj), is found by using the diffusivity of the material at the furnace temperature. The chemical reaction for the oxidation of the POCI₃ is as follows:

\[
4\text{POCl}_3 + 3\text{O}_2 \rightarrow 2\text{P}_2\text{O}_5 + 6\text{Cl}_2
\]

\[
4\text{P}_2\text{O}_5 + 5\text{Si} \rightarrow 4\text{P} + 5\text{SiO}_2
\]

PROCESS PERFORMANCE
The amount of dopant entering the diffusion tube must be controlled so that resistivity, process uniformity and repeatability are maintained. This control is achieved by maintaining a constant temperature for the chemical and accurate control of the carrier gas flow rate through the bubbler. Figure 1 is the vapor pressure curve for the material. The most common bubbler temperature used is 20°C. It is necessary to maintain the bubbler temperature at least 5°C lower in temperature than the surrounding temperature of the air around the tubing that connects the bubbler to the furnace. This prevents the formation of condensation in the line leading from the bubbler to the diffusion tube. It is also important to make sure that the temperature chosen for the chemical will allow the operation of the gas controller within the calibration range of the unit. This is important when using thermal mass flow gas controllers.
SELECTION OF CARRIER GAS
The most common carrier gas that is used in the industry is nitrogen. Argon can also be used as a carrier gas for the chemical if it is desirable to use a true inert gas. Under no condition should oxygen ever be used as a carrier gas for this chemical. This is a very unsafe practice that in the past was common within the industry. Such practice can cause the failure of the bubbler and loss of containment of the chemical. The selection of an inert carrier gas is advisable for safe operation. Pick up rates for the material is independent of the carrier gas.

CHEMICAL MASS FLOW RATES
Figure 2 is the POCI₃ pickup rate at various carrier gas flow rates and bubbler temperatures. These values are calculated using the following equation:

\[ M_{\text{POCl}_3} = \left( \frac{P_{\text{vap}}}{P_b - P_{\text{vap}}} \right) \cdot [\text{Q}_{\text{PCC}} \cdot \left( \frac{\text{MW}}{22414} \right)] \]

Where:
- \( O(M_{\text{POCl}_3}) \) = POCI₃ Pickup Rate in grams per minute.
- \( P_{\text{vap}} \) = POCI₃ Vapor Pressure (torr) at bubbler temperature.
- \( P_b \) = Pressure in bubbler (atmospheric pressure in torr at FAB location altitude above sea level).
- MW = Molecular Weight of chemical (POCl₃=153.33 g/g-mole).
- \( Q_{\text{PCC}} \) = Carrier Flow at SCCM.
SETTING UP THE PROCESS

The first step in setting up a POCI₃ process is to find the actual volume of the tube. This is done by using the following equation:

\[ V = \frac{\pi r^2 L}{1000} \]

Where:

- \( V \) = total volume of the tube in Liters
- \( \pi \) = 3.1416
- \( r \) = radius of the diffusion tube in centimeters
- \( L \) = length of the diffusion tube in centimeters

Using the example of a tube 14cm in diameter and 215.9cm in length as a tube that will be used for a deposition process, the following steps should be used to decide the three gas flow ranges.

1. Find the volume of the tube using the equation listed above. The radius is 7.0cm and the length is 215.9cm therefore the volume is \((3.1416 \times 49.0 \times 215.9) \div 1000 = 33.24\) liters. This represents the total volume of the tube that is going to be used for the POCI₃ deposition.

2. Decide what exchange rate of the gas will be needed for the process. The exchange rate of the gas should be between 3 (Three) minutes and 7 (Seven) minutes. This will provide an adequate source of new material to the wafer surface. The exchange rate is also set by the source flow time used for the deposition. This information is found later in the discussion at Figure 4. Some adjustment to the exchange rate may be made later in the discussion. As a practical note, an exchange rate of 5 (Five) minutes will prove to be best for most furnace set ups. Five minutes will be used in this example.

3. Now divide the volume of the tube by the exchange rate and find the answer. Using the volume in step 1 as the example, the answer is 33.24 divided by 5 equals 6.65 liters per minute of Main nitrogen gas flow.

4. Find the amount of Oxygen needed for the process by calculating 5% of the 6.65 liter main nitrogen flow. The answer of 0.332 liters per minute, is the amount of oxygen flow that is needed to react all of the chemical by providing the oxidizing ambient.

5. Find the amount of carrier gas needed for the process by calculating 5% of the 6.65 liter main nitrogen flow or again 0.332 SLM of carrier flow. The 5% is used to find the carrier flow at a bubbler temperature of 20°C. This would result in a carrier flow of 0.332 SLM. For other bubbler temperatures use Figure 3 to find the actual percentage that must be used.

Fig. 3—Other Bubbler Temperatures
Main Nitrogen = 6.65 SLM  
Oxygen Flow = 0.332 SLM  
Carrier Nitrogen Flow = 0.332 SLM at 20°C

The final correction that must be made to the carrier gas flow is the adjustment for elevation above sea level. The elevation above sea level does affect the saturation point. Unless this correction is made, the difference to the carrier gas flow will be large enough to create problems. This can result in process difficulties when gas flows are moved from one plant site to another location, when there is a difference in elevation. From Figure 4 this correction will be used to reduce the carrier flow as the height above sea level increases. Figure 4 provides a quick correction to the flow without recalculation of the actual mass flow. This correction to the carrier gas flow rate will ensure that any change in elevation will produce the same furnace gas flow condition. It is necessary to make this correction to find the actual mass flow of dopant going into the process furnace. As a rough approximation, the pressure drops by lmm for a change of 40.6 feet in elevation above sea level.

The only information missing at this point is the actual source running time in minutes that the carrier will be bubbling and the temperature needed to operate the furnace to produce the desired resistivity deposition. To solve the last two unknowns, it is necessary to look at the Solid Solubility at various temperatures for Phosphorus in Silicon.

<table>
<thead>
<tr>
<th>Solid Solubility of Phosphorus in Silicon at Various Temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200°C = 1.0 X 10^21</td>
</tr>
<tr>
<td>1150°C = 1.4 X 10^21</td>
</tr>
<tr>
<td>1100°C = 1.2 X 10^21</td>
</tr>
<tr>
<td>1050°C = 9.0 X 10^20</td>
</tr>
<tr>
<td>1000°C = 8.5 X 10^20</td>
</tr>
<tr>
<td>950°C = 6.8 X 10^10</td>
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<tr>
<td>900°C = 5.0 X 10^10</td>
</tr>
<tr>
<td>850°C = 3.5 X 10^10</td>
</tr>
<tr>
<td>800°C = 2.0 X 10^10</td>
</tr>
</tbody>
</table>

The source of the data is; BELL SYSTEM TECHNICAL JOURNAL #39; 1960 PAGE 205 by F.A. Trumbore. The information suggests the maximum will be reached at 1150°C and drops at higher temperatures. This information can be used to arrive at ranges for the various furnace temperatures based on the amount of source flow time.
This general information can provide a rough starting point for the process. The overlap of the resistivity range is due to the difference in the time that the source is on. Time in each range varies from 5 minutes to 50 minutes of source flow time. Using this information, curves can be developed that will cover the range in greater detail. This information is shown in Figure 5. In all examples that will be given, the source cycle will consist of the following:

![Figure 5](image)

**SAMPLE PROCESSES**

The following single sequence processes are provided as examples only and are intended to provide a starting point for process development. The information and formulas given are for the average cantilevered wafer support system. Should any other type system be in use, it may be necessary to modify the total gas flows for this type of system. However, the ratio of source gas flow to main nitrogen gas flow and that of the oxygen gas flow must be kept constant. Some adjustments to the flows may also be necessary to obtain the best resistivity control across the wafer and run to run. This is the art of fine tuning the process. For use as an example, the assumptions that will be made are as follows:

1. Wafer diameters of 125mm to 150mm
2. Tube diameters of 190mm and 235mm corresponding to the matching wafer diameters
3. Tube length of 1.829 meters
4. Target sheet resistivity reading of 3-5 per square
5. Bubbler temperature of 20°C
6. Elevation assumption is sea level (760mm Hg)

Using the information from the text, the first step is the determination of the volume of the tube. The volume of the 190mm x 1.829m tube is 51.86 liters. Using a gas exchange rate of once every 5 minutes, the nitrogen needed is 10.4 SLM. The next step is to decide the oxygen flow. Using the information given we find that 5% of the main nitrogen flow is 0.519 SLM. This is the correct amount of oxygen for the process. The source nitrogen flow, because the bubbler temperature is 20°C, will be the same percentage as the oxygen flow, or 0.519 SLM. If another bubbler temperature was going to be used, the percentage would have been changed to the correct amount shown in Figure 3. The same logic is used for the larger tube. Putting the information in chart form the processes are as follows:

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>OHM per Square</th>
</tr>
</thead>
<tbody>
<tr>
<td>835</td>
<td>50 - 100</td>
</tr>
<tr>
<td>850</td>
<td>38 - 100</td>
</tr>
<tr>
<td>900</td>
<td>15 - 40</td>
</tr>
<tr>
<td>950</td>
<td>6 - 20</td>
</tr>
<tr>
<td>1000</td>
<td>3 - 10</td>
</tr>
<tr>
<td>1050</td>
<td>2 - 6</td>
</tr>
<tr>
<td>1100</td>
<td>1 - 3</td>
</tr>
</tbody>
</table>
NOTE: The Purge and Soak times are not less than the exchange rate of the system. This is important to keep both times longer than the gas exchange time. By keeping the time longer, this will prevent problems with uneven distribution of the dopant down the furnace tube length. There are several combinations of furnace temperature and source times that will allow one to hit the desired resistivity.

The important point to remember is the entire thermal budget of the process. Sometimes it may be important to go to a higher temperature for a short source time. Other times it may be beneficial to have low temperature and long source times to reduce the thermal budget of the process. These are the fine points of process design and development.

*NOTE: The purge cycle may be run with an atmosphere of pure Oxygen to reduce the Phosphorus concentration in the deposited glass layer on the wafer surface. This reduction in concentration will reduce the problem of poor adhesion that could be experienced at photo masking and will be helpful in reducing the build up on the quartzware. The actual purge cycle could be operated with any combination of Oxygen and Nitrogen. The larger the amount of Oxygen, with respect to the Nitrogen flow, will result in a surface oxide that will be less prone to absorb moisture. Again, this is part of the individual development steps that are device dependent.

The information presented here is of a general nature that if followed will produce a working set of furnace conditions. These conditions can then be refined by the process engineer to develop a process that will be tailored to a unique set of conditions. This information, as presented will produce starting points and not final process conditions.
SPECIAL NOTES

1. Wafers are mounted perpendicular to the flow of gas. The direction of the active side of the wafers should be facing the source during the initial set up of the process. The direction may be changed to facing away from the source to see if this helps uniformity.

2. The load size of Silicon wafers must be the same for each run. Dummy or non process wafers must be placed in all vacant slots to completely fill the boat. All freshly stripped dummy wafers or new wafers should be pre-sourced by running them through one or more process cycles before using them with product wafers. Failure to perform this step could result in poor uniformity.

3. Placement of the wafers into the furnace must be done so that the space around the wafers to the furnace tube wall is equal distance all the way around. There must not be an area of uneven spacing. This step is important to obtain good resistivity control across the wafers.

4. Wafer spacing is three sixteenths of an inch or 4.7mm center to center. The wafers must not touch one another.

5. All process gas must have low moisture content. The gas should have less than 1.0 ppm of water content. Not only will contamination of the chemical result with time, but the control of the process parameters will be unpredictable. To produce a stable process, the moisture content of the process gas supply must be kept constant, and at the lowest possible amount. Moisture which enters the gas supply is the single largest cause of process upsets. It is important to measure the moisture content of all gas supplies at the point closest to where the gas enters the diffusion tube. A moisture monitor should be installed near the point of use, as close to the jungle as possible. Gas lines do develop leaks with time and it should never be taken for granted that the gas is free from moisture contamination.

6. All gas lines must be leak tight. All connections between the source of the gas and the final use point must be leak free.

7. Due to the reaction of the exit gas from the furnace with the moisture in the scavenger section, there will be a build up of a viscous clear material at the end of the tube. This can be eliminated by reducing the flows of the chemical used in the process, or by heating the chilled end of the tube from the last heater element to the exit exhaust. There are special heater blocks that can be used that will stop the accumulation of the acid at the end of the tube. This material is composed of mainly phosphoric acid and small amounts of hydrochloric acid. This material should be handled using standard acid handling techniques.

8. Cleaning of all quartz should be done on a regular basis to eliminate the build-up of phosphorus on the walls of the tube. This build-up is not as pure phosphorus but as a heavily doped phosphorus silicate glass. Because this material can act as a source of phosphorus to the wafers it must be removed by chemical means. This is done by using dilute solutions of HF and water. The mixture that is used most common is 10 to 1 or 10 parts water to 1 part HF. This step is done under a hood with the correct safety gear being worn. After the cleaning, the quartz must be pre-sourced to prevent the quartz from becoming a sink for the dopant. Failure to perform this step will result in uniformity problems to the first wafers processed after the cleaning cycle.

9. Another method of keeping the furnace free of the build up is to steam the tube occasionally. This is done by using an oxygen/hydrogen injector to form the steam in the furnace tube. This is simple to set up when new furnaces are installed or if the jungles are being replaced with new designs. By using this type of process, the life or use of the tube is extended between regular pull and clean operations. This method has been used to extend the actual pulled time to only two events per year. This increases the actual production output of the furnace. Another method is to place the furnace into standby using pure oxygen atmosphere in place of the usual nitrogen. This will also reduce the amount of buildup dopant in the tube.

10. Phosphorus Oxychloride will react with water in a violent manner. Contact between this chemical and water should be avoided. Should a spill happen, the material should be absorbed with the proper absorbent material. This material must be compatible with the location it is going to be used in, and the chemical. Materials such as vermiculite can absorb the chemical but the dust and the sodium may be a problem to most Fabs. For proper material selections please consult your Safety Department. Safe handling of the material is dependent on the location of the Fab and the individual safety departments and environmental regulations in each area.
11. The maximum flow rate for the bubbler size that is installed must not be exceeded. The maximum flow that is recommended for the 500cc bubbler is 400 SCCM. The larger 1000cc and 1500cc bubblers will operate with the flows as high as 2000 SCCM or 2 SLM.

12. The bubbler must not be exposed to a pressure greater than 15 PSIG.

13. To reduce surface damage a small thickness of silicon dioxide may be grown over the exposed silicon surface prior to dopant deposition. Care must be taken in determination of the proper thickness of this layer. The thickness must not mask the dopant. In general, the thickness will be less than 100Å.

The information that remains to be learned, the calculation of the depth of the diffused material. The junction depth \(X_j\) is a function of the temperature, material starting resistivity and the time that the wafers are at the diffusion temperature. This subject is well covered in many process engineering books.

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.