PhosPlus

High-Purity Planar Dopant Sources

ISO CERTIFIED 9002/14001
Diffusion Sources:

Produce pure depositions.
- The use of high-purity raw materials results in high-purity doping of single crystal or polysilicon wafers.

Give uniform sheet resistivities.
- Uniformities typical of the planar diffusion depositions (2% across the silicon, 3% across the boat and 4% run-to-run) or better can be achieved on both single crystal and polysilicon wafers.

Exhibit long lifetimes.
- Hundreds of use-hours have been reported by various users.

Are safe to use.
- The sources are noncorrosive and nontoxic.

Simplify the process.
- Require no complex metering equipment commonly associated with gas and liquid dopants.
- Exhibit a minimum of water absorption.
- Need no periodic reactivation cycles.
- Can be used from 800°C to 1150°C.
- Can be removed from diffusion boats for periodic boat deglazing.
- Are compatible with many automatic transfer systems.

Minimize silicon damage.
- Many users have obtained less silicon damage on wafers doped with PhosPlus sources than other n-type diffusion techniques.
- Produce smooth polysilicon layers for double layer applications.
**PhosPlus® Planar Dopant Sources Have Widespread Uses.**

PhosPlus planar diffusion sources represent a significant advancement in the field of phosphorus dopant materials. Their ability to easily and uniformly dope large-diameter silicon wafers in a safe manner accounts for their increasing popularity in the semiconductor industry. In general, PhosPlus sources offer all the advantages traditionally associated with planar sources plus they possess a number of additional improvements which make them the most desired phosphorus source available to the diffusion engineer.

**Two PhosPlus Sources Provide Versatility.**

Two PhosPlus sources are available to meet the many silicon processing requirements of the semiconductor industry. The following temperature ranges are normally recommended for their use:

<table>
<thead>
<tr>
<th>Source Type</th>
<th>Recommended Temperature Range, °C</th>
<th>Approximate Sheet Resistivity, Ω/□</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP-470</td>
<td>950-1150</td>
<td>&lt;1-7</td>
</tr>
<tr>
<td>TP-250</td>
<td>800-950</td>
<td>5-100</td>
</tr>
</tbody>
</table>

Each type of PhosPlus source contains P₂O₅ and the extremely stable oxides of Ta₂O₅, Al₂O₃, and/or La₂O₃. The sources are manufactured in such a way that the P₂O₅ is combined with Al₂O₃ or La₂O₃, and it only evolves when the sources are heated to the doping temperatures through one of the following decomposition reactions:

- **TP-470**
  
  \[ \text{Al}(\text{PO}_3)_3 \rightarrow \text{AlPO}_4 + \text{P}_2\text{O}_5 \]

- **TP-250**
  
  \[ \text{LaP}_5\text{O}_{14} \rightarrow \text{LaP}_3\text{O}_9 + \text{P}_2\text{O}_5 \]

Several thin radial slots are cut into the sources to ensure that they will not fracture when rapidly heated in the diffusion furnace. The slots have no effect on the uniformity of the doped silicon wafer. The TP-470 sources also contain Ta₂O₅ to adjust their thermal expansion coefficients and make them extremely resistant to thermal shock.

**Exhibit High Purity.**

The PhosPlus sources are manufactured from raw materials exhibiting very high purity. These materials are made using special processing techniques developed at TECHNEGLAS, Inc. A typical impurity analysis of a source when measured on a spark source mass spectograph is given in Table I.

**Are Safe to Use.**

PhosPlus sources are made of materials that are nontoxic, and they evolve only P₂O₅ during use. Special safety equipment and alarm systems that detect very low levels of highly toxic gases, therefore, are not required.
A second method of estimating the lifetime of a source is to measure the amount of weight a source loses at a use temperature as the P$_2$O$_5$ evolves. Weight loss data for the TP-470 sources (Figure 2) indicate a continuing process of P$_2$O$_5$ evolution over hundreds of use hours.

**Doping Properties of PhosPlus Sources.**

**Single Crystal Silicon:** Typical sheet resistivity versus deposition time curves for the two PhosPlus sources are plotted in Figures 5 and 6. The curves are different for each source because the sheet resistivity of the silicon wafer for a given deposition cycle depends somewhat upon the thickness of the deposited glassy film. The thicker the glassy film, the lower the sheet resistivity. Figure 7 shows how the deposited film thickness varies with the type of source being used.

---

**Figure 2**

**Figure 3**

**Figure 4**

**Figure 5**

**Figure 6**

**Figure 7**
A typical deposition time for a solid-source diffusion system is about 45 minutes. This time is usually long enough for the sources to uniformly dope the silicon wafers. At the same time, it is short enough to be compatible with most semiconductor process parameters. Figure 8 shows the sheet resistivity and junction depth that is obtained from a 45-minute deposition with the TP-470 PhosPlus sources at various deposition temperatures.

**Doping Properties of PhosPlus Sources.**

**Polysilicon:** The minimum sheet resistivity that can be obtained from polysilicon wafers that are saturated with phosphorus partially depends upon the thickness of the polysilicon layer as shown in Figure 9. These sheet resistivities are about 12 Ω/sq for 5000Å of polysilicon and about 32 Ω/sq for 2500Å, and they occur when the deposited phosphorus glassy film exceeds about 500 to 600Å as shown in Fig. 10. Glassy films that are less than 500Å can also be uniformly deposited on the polysilicon wafers from the PhosPlus sources to produce higher sheet resistivities for special applications. Figure 10 can be used as a guide to determine the approximate thickness that is required for different sheet resistivities.

Doped polysilicon layers with smooth surfaces are important in the manufacture of certain devices. Very smooth surfaces can be obtained when the polysilicon layer is first doped with the TP-250 sources to a level slightly below saturation (400-500Å as shown in Fig. 10). When this glass is etched off and the silicon wafers are annealed near 950°C for about 15 min, smooth surfaces are maintained and the silicon exhibits the minimum sheet resistivity characteristic of its thickness (Fig. 9).

Sheet resistivities at or above the saturation of phosphorus in polysilicon can be obtained from either phosphorus source. The appropriate deposition cycle can be selected from the curves shown in Figures 11 and 12.
Doping Properties of PhosPlus Sources.

Uniformities: When the various processing conditions are optimized, uniformities of 2% across the silicon, 3% across the boat and 4% run-to-run or better can generally be obtained on single-crystal silicon. A total variation of about 3% can be achieved on high-quality polysilicon wafers doped to their minimum sheet resistivities (saturation with phosphorus).

These uniformities are quite typical of the planar diffusion system and tend to be independent of the diameter of the wafer and the number of silicon wafers being processed during a run. This independence can result in an increase in silicon throughput compared to the number of silicon wafers often processed in gas systems. It can also significantly increase production yields by improving process control as demonstrated by the decrease in beta variation when TP-470 PhosPlus sources are used for an emitter diffusion instead of POCl₃ (Figure 13).

Preparing and Storing PhosPlus Sources:

Cleaning: As part of the routine cleaning process, the PhosPlus sources are acid etched to remove any foreign matter and to expose a pristine surface. As a result, no additional cleaning is necessary before putting the sources into the diffusion furnace. If additional cleaning is desired, the procedure in Table II is the only one recommended.

Preparation: Before using the PhosPlus sources in production for the first time, they should be held at the intended deposition temperature for a period of time. This will ensure that all moisture has been vaporized, and it enables the sources to achieve a constant P₂O₅ evolution rate. The aging period may last from a few hours for high temperature processes to as long as 24 hours for low temperature processes. Figure 14 gives the recommended minimum aging times for the two PhosPlus sources.

Storage: Since the phosphorus is present within the sources in the form of a complex crystal and not as the extremely hygroscopic P₂O₅ material, the PhosPlus sources exhibit a minimum amount of water absorption. However, the absorption of even small amounts of moisture can cause various problems in silicon processing. It is therefore recommended that the sources be stored in the diffusion boats in nitrogen at an elevated temperature when the time between runs exceeds about 45 minutes. If the sources were accidently left out in a room for a long period of time, however, they can be quickly prepared for the next run by merely inserting them into the diffusion tube at the insertion temperature for about 15 minutes. When they are withdrawn from the tube, the boat is ready for loading with production silicon.

Preparing and Storing PhosPlus Sources:

Cleaning: As part of the routine cleaning process, the PhosPlus sources are acid etched to remove any foreign matter and to expose a pristine surface. As a result, no additional cleaning is necessary before putting the sources into the diffusion furnace. If additional cleaning is desired, the procedure in Table II is the only one recommended.

Preparation: Before using the PhosPlus sources in production for the first time, they should be held at the intended deposition temperature for a period of time. This will ensure that all moisture has been vaporized, and it enables the sources to achieve a constant P₂O₅ evolution rate. The aging period may last from a few hours for high temperature processes to as long as 24 hours for low temperature processes. Figure 14 gives the recommended minimum aging times for the two PhosPlus sources.

Storage: Since the phosphorus is present within the sources in the form of a complex crystal and not as the extremely hygroscopic P₂O₅ material, the PhosPlus sources exhibit a minimum amount of water absorption. However, the absorption of even small amounts of moisture can cause various problems in silicon processing. It is therefore recommended that the sources be stored in the diffusion boats in nitrogen at an elevated temperature when the time between runs exceeds about 45 minutes. If the sources were accidently left out in a room for a long period of time, however, they can be quickly prepared for the next run by merely inserting them into the diffusion tube at the insertion temperature for about 15 minutes. When they are withdrawn from the tube, the boat is ready for loading with production silicon.

Preparing and Storing PhosPlus Sources:

Cleaning: As part of the routine cleaning process, the PhosPlus sources are acid etched to remove any foreign matter and to expose a pristine surface. As a result, no additional cleaning is necessary before putting the sources into the diffusion furnace. If additional cleaning is desired, the procedure in Table II is the only one recommended.

Preparation: Before using the PhosPlus sources in production for the first time, they should be held at the intended deposition temperature for a period of time. This will ensure that all moisture has been vaporized, and it enables the sources to achieve a constant P₂O₅ evolution rate. The aging period may last from a few hours for high temperature processes to as long as 24 hours for low temperature processes. Figure 14 gives the recommended minimum aging times for the two PhosPlus sources.

Storage: Since the phosphorus is present within the sources in the form of a complex crystal and not as the extremely hygroscopic P₂O₅ material, the PhosPlus sources exhibit a minimum amount of water absorption. However, the absorption of even small amounts of moisture can cause various problems in silicon processing. It is therefore recommended that the sources be stored in the diffusion boats in nitrogen at an elevated temperature when the time between runs exceeds about 45 minutes. If the sources were accidently left out in a room for a long period of time, however, they can be quickly prepared for the next run by merely inserting them into the diffusion tube at the insertion temperature for about 15 minutes. When they are withdrawn from the tube, the boat is ready for loading with production silicon.
Typical Doping Procedures with PhosPlus Sources.

**Boats:** Although diffusion boats of various designs have been successfully used with the PhosPlus sources, the best results are normally obtained with a four-rail quartz boat having a design as shown in Figure 15. When depositions are made above 1100°C, silicon carbide or polysilicon boats are often preferred because of their increased resistance to deformation. Boats made of any of these materials fit on standard paddles and cantilever systems and can be used in automatic transfer systems. The spacing between the silicon surface and the source surface should be constant and should be between 0.060" and 0.100". The slots for the sources should be about 0.010" wider than their thickness. The sources should fit loosely in the boat, allowing room for expansion of at least 0.010" per inch of diameter.

**Insertion and Removal:** A furnace ramping technique should be utilized for all deposition cycles. This procedure involves slowly inserting the boatload of wafers into the diffusion tube at a temperature below about 800°C and at least 100°C less than the deposition temperature. After the furnace and boat have reached thermal equilibrium, the furnace is ramped to the deposition temperature. At the end of the deposition time, the furnace is cooled back to the insertion temperature, at which time the boat is withdrawn. The insertion and withdrawal rates should not be more than 4 in./min. for 100 mm sources. Because of the greater mass of material involved, slower insertion and withdrawal rates should be used with the larger diameter sources.

**Ambient Gases:** Either of the two PhosPlus sources can be used with the conventional gases of nitrogen or argon without detrimentally affecting their doping performance. Although oxygen does not adversely affect the sources, too high of an oxygen concentration should be avoided because of the potential for masking off the silicon surface to be doped. Steam should also be avoided in the presence of the PhosPlus sources at the deposition temperature. Steam causes the P₂O₅ to rapidly evolve from the sources resulting in shorter lifetimes of the sources.

When using the TP-470 sources above 1000°C, small quantities of oxygen may be blended with the nitrogen or argon. The oxygen concentration in the carrier gas is usually less than 1% below 1050°C and could be as high as 5% at temperatures above 1100°C.

When the TP-250 sources are used near 900°C, the oxygen concentration should be maintained below about 1%. This concentration may be increased up to about 5% when depositions are made at higher temperatures. No oxygen should be used below about 875°C, especially when polysilicon layers are being doped.

**Gas Flow Rates:** The gas flow rate utilized during the deposition depends primarily upon the diffusion equipment such as tube size and end cap design. Although the flow rate must be high enough to prevent room air from backstreaming down the diffusion tube, flow rates ranging from as low as 2.0 l/min. to as high as 15 l/min. have been successfully used in a 135 mm diffusion tube. Satisfactory results are most often obtained with a flow rate of 3-7 l/min. for this tube size.
PhosPlus ® planar diffusion sources are available in sizes up to 200mm in diameter. For further information on these materials, contact:

TECHNEGLAS
TECHNICAL PRODUCTS

25875 S.R. 25, 52 LDP
Perrysburg, Ohio 43551
(419) 873-2000
FAX: (419) 873-2020
www.techneglas.com
e-mail: dopants@techneglas.com