From Sand To Silicon Wafer

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INTRODUCTION

In the semiconductor industry, there are basically ten global industrial sectors considered in the production chain of high quality semiconductors. These sectors are the one involved in producing quartz/silica (SiO_2), coal, charcoal, silicon metal, chlorosilane compound (chemical used in purifying silicon), polycrystalline silicon (polysilicon), semiconductor devices, solar cells and optical fibers. Figure 2 shows how these industrial sectors are related to each other (Williams, 2000).

Silicon wafers are the main materials for the fabrication of integrated circuits. The production of silicon wafers starts off with polycrystalline silicon (polysilicon). The polysilicon is converted into monocrystalline silicon (monosilicon) ingot form before it can be used to make silicon wafers. Monosilicon ingots are usually produced by either the Czochralski (CZ) method, or the Float Zone (FZ) method (Williams, 2000). A simplified process flow of how integrated circuit is produced from raw materials is shown in Fig. 3.

Solar-cell grade silicon (SGS) and the electronic grade silicon (EGS) are two of the grades commonly used to characterize polysilicon. The purity of solar-cell grade polysilicon is known as six 9's (six nine) while the purity of electronic grade polysilicon is generally known as eleven 9's (eleven nine) (Williams, 2000).

Polysilicon production is a highly specialized industry and essentially its only application is in producing silicon wafers for semiconductors and solar cells. There are about 8 to10 major manufacturers of polysilicon in the world and some smaller producers in the East European countries (AFOSR, 1997). USA , Japan and Germany are the three major producers of polysilicon in the world (Yamauchi, 1998).

Technologies for producing polysilicon ingot are based on the feedstock technology. The four main feedstocks are listed as follows.

- Silicon tetrachloride (Siemens process)
- Trichlorosilane (Siemens process)
- Dichlorosilane (Siemens process)
- Silane (ASiMI process)

A detail discussion of the processes can be found in the references (Rogers, 1990; ASiMI, 1999).

The main raw or starting material which is the metallurgical grade silicon (MGS) is obtained from Elkem in Norway. The purity of the MGS is about 98%.

Prior to characterization, the polysilicon sample will be converted to single crystal silicon ingot. The resultant single crystal ingots are then analyzed by spectrophotometric methods to determine the trace impurities in the polysilicon. These trace impurities are acceptor (usually boron or aluminum, or both), donor (usually phosphorus or arsenic, or both), and carbon impurities (ASTM, 2001).

POLYSILICON PRODUCTION OVERVIEW

The production of polysilicon requires several distillation steps and it is known that more than 98% of electronic grade polysilicon is produced by the trichlorosilane ($SiHCl_3$) distillation method (Rogers, 1990; Frank et. al., 1996). The process of obtaining electronic-grade polysilicon starts with the reduction of quartzite or silica to MGS. A summary of the process involve is shown as follows.

(i) Quartzite to metallurgical-grade silicon:

During the process, SiO_2 is decomposed into metallurgical-grade silicon and carbon monoxide, according to the carbothermic reaction (Suzuki, 1998; Nagamuri et. al.,1986):

$$SiO_2\,(s) + 2C\,(s) \rightarrow Si\,(s) + 2CO\,(g) \qquad (1)$$

(ii) MGS to trichlorosilane:

Crude MGS must undergo rigorous purification to reach a purity level suitable for semiconductor device applications. The standard process used is the reaction of MGS with hydrogen chloride, HCl to form SiHCl3. The following shows the main reaction of MGS with HCl to form SiHCl3 (Chu, 2001).

$$Si\,(s) + 3HCl\,(g) \rightarrow SiHCl_3\,(g) + H_2\,(g) \qquad (2)$$

(iii) Distillation of trichlorosilane (SiHCl3)

Dissolved trichlorosilane at room temperature is then purified by distillation process. This is the main purification step for the electronic grade silicon (EGS) and the resulting impurity levels are at a few parts/billion atomic (ppb). The impurities which remain in the purified $SiHCl_3$ are SiH_2Cl_2, $SiCl_4$, C, Fe, Ca, and Al (Jackson, 1996).

(iv) Electronic-grade polysilicon

Once the purified $SiHCl_3$ is obtained, it is then used to deposit very pure polysilicon onto a thin monosilicon seed that serves as a starting material in a chemical vapour deposition (CVD) reactor. The main reaction for the production of polysilicon is shown below.

$$SiHCl_3\,(g) + H_2\,(g) \rightarrow Si\,(s) + 3HCl\,(g) \qquad (3)$$

POLYSILICON GROWTH IN CHEMICAL VAPOUR DEPOSITION SYSTEM

Figure 4 shows the polysilicon production scheme used in the actual polysilicon plant at GAO Kristall. Some other sub-plants which are not shown in Figure 4 are the steam plant, water circulation pump plant, water treatment plant, energy block plant, air separation plant and neutralization plant. The starting raw materials which are not produced on-site are chlorine gas (Cl_2) and MGS or silicon metal. Hydrogen chloride (HCl) which is produced on-site using H_2 and Cl_2, together with MGS are processed in the TCS (trichlorosilane) plant to produce $SiHCl_3$ and $SiCl_4$.

Liquid $SiHCl_3$ which vaporise at temperatures between 30°C to 32°C (Chu, 2001) goes into a vaporizer where it will form SiHCl3 gas by boiling it at a temperature above 30°C. Hydrogen gas, H_2 is usually obtained via electrolysis of water and goes through a purification process normally by using palladium (Bretschneider, 2001), platinum (NRCC, 2001) or chrome nickel (GAO, 2001) filters. Both $SiHCl_3$ and H_2 gases are then channeled into a CVD reactor where the main reaction takes place. High current, up to 2 kA will flow between the cathode and anode of the silicon seed where the seed's temperature is allowed to reach between 1050°C and 1150°C. A pyrometer is used to measure the temperature of the polysilicon rod during deposition.

During the deposition process, by-products are continuously pumped out and condensed into liquid form. These by-products are directed to the purification plant where they will be separated into useful gases and recycled. Material such as $SiCl_4$ is used for producing quartz whereas H_2, HCl and other silane compounds will be refined and re-used in the plant. Marketable by-product of the polysilicon plant are the quartz tube (from $SiCl_4$), and H_2. $SiCl_4$ is also used in the fabrication of fiber optics cable.

POLYSILICON CHARACTERISATION

Evaluation of polysilicon rods is done by a suitable method as recommended by American Society for Testing and Materials (ASTM). These rods are not tested directly but are usually converted to monosilicon and finally analyzed using spectrophotometric methods to determine the trace impurities in them.

The ASTM F1723-96 (formerly known as F574) recommends the procedures for sampling polysilicon rods and growing monosilicon from the polysilicon samples by the Float-zone method (ASTM, 2001). In the F1723-96 standard, the three main impurities tested for are the donor, acceptor and carbon impurities. Additional test will be done for oxygen content, resistivity and carrier lifetime (Perkin Elmer, 2001). Table 1 shows the main impurities and standards used for analyzing them (ASTM, 2001; PerkinElmer, 2001). (See Table 1)

The useful range of impurity concentration covered by this practice is 0.002 to 100 parts/billion atomic (ppb) for acceptor and donor impurities, and 0.05 to 5 parts/million atomic (ppm) for carbon impurity. Several other impurities were also measured which includes iron (Fe), chromium (Cr), nickel (Ni), copper (Cu), zinc (Zn), and antimony (Sb). The range of impurity concentration covered by this practice is still in the ppb range while the useful range for oxygen is 0.01 ppm. Resistivity test is usually done where the recommended value is about 80,000 ohm-cm.

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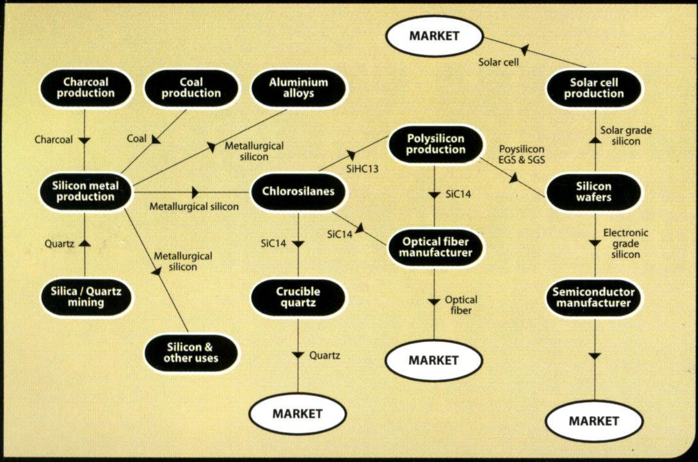

Figure 2: Production chain for high-purity silicon and its use in semiconductors, solar cells and optical fiber

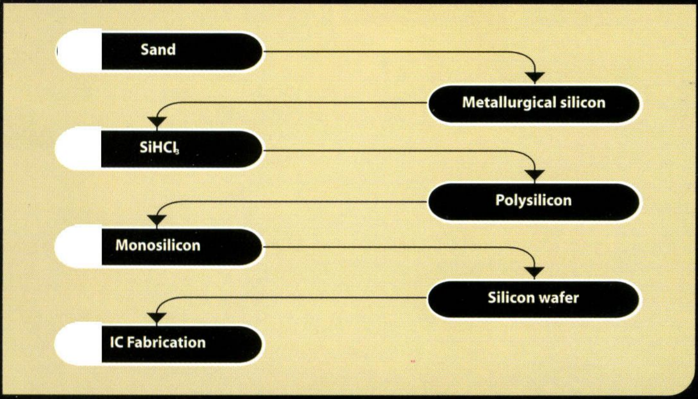

Figure 3: Raw material to IC fabrication process flow

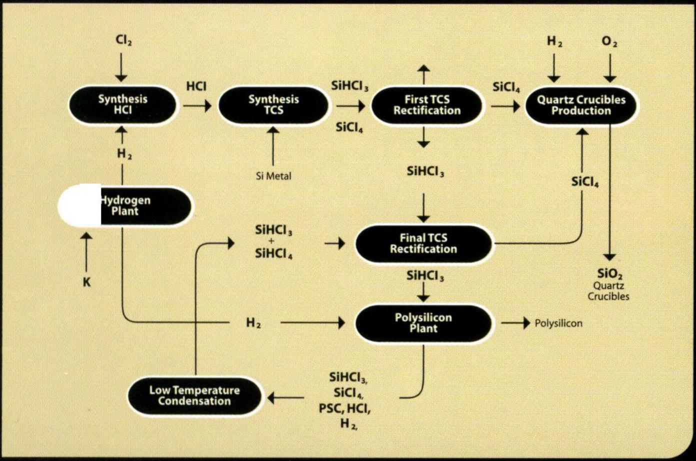

Figure 4: GAO Kristall polysilicon production scheme