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Contributed Paper

High Purity Polycrystalline Silicon Growth and Characterization

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ABSTRACT

Polysilicon is the main raw material in making silicon wafers in which integrated circuits are made of. The polysilicon production chains start off with high purity sand which is decomposed into metallurgical-grade silicon (MGS). The reaction of MGS with hydrogen chloride (HCl) will form trichlorosilane ($SiHCl_3$) which then goes through several purification steps in order to obtain pure $SiHCl_3$. The subsequent reaction of $SiHCl_3$ and H_2 in a chemical vapour deposition (CVD) reactor will deposit very pure polysilicon onto a thin monosilicon seed rod. The polysilicon samples were sent for testing at an independent laboratory and analyzed using XRF spectroscopy to determine the main impurities of P, B, O and C. Several other impurities were also measured which includes Fe, Cr, Ni, Cu, Zn, and Sb. Based on the measurement of the impurity concentrations, the purity of the polysilicon is at 99.9995% which is below the requirement for an electronic-grade polysilicon which is 99.999999999%. Resistivity measurement shows a high concentration of P content which indicates that it is an n-type polysilicon.

Keywords : polysilicon, trichlorosilane, czochralski (CZ) method, float zone (FZ), solar cell grade silicon (SGS), electronic grade silicon (EGS).

1. INTRODUCTION

Silicon wafer is the main starting material for the fabrication of integrated circuits as we know today. The main material for producing silicon wafers is the polycrystalline silicon (polysilicon). Polysilicon will be converted into monosilicon ingot form before it can be used to make silicon wafers. There are currently two methods of producing monosilicon ingots which is by the Czochralski (CZ) method, and the Float Zone (FZ) method [1]. A simplified process flow of how integrated circuit is produced from raw materials is shown in Figure 1.

Two common grades of polysilicon which is used for grading the quality of the polysilicon are the solar-cell grade silicon (SGS) and the electronic grade silicon (EGS). 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) [1].

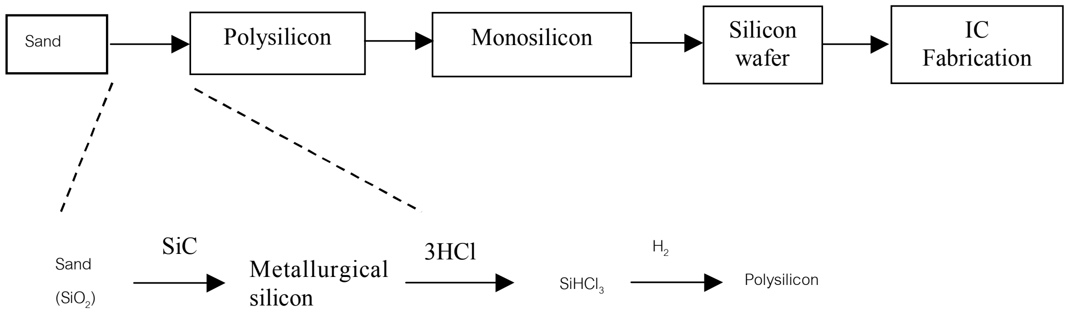

Figure 1. From sand to IC fabrication process flow.

Polysilicon production is a highly specialized industry and essentially its only application is in producing silicon wafers for semiconductors and solar cells. Technologies for producing polysilicon ingot are based on the feedstock technology. The four main feedstocks are as follows. A detail discussion of the processes can be found in reference [2].

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

Around 80% of the world polysilicon production uses the Siemens process which utilizes trichlorosilane [3]. The main starting material which is the metallurgical grade silicon (MGS) is obtained from Elkem in Norway where the purity of the MGS is about 98%.

Before the polysilicons are characterized and tested, they will be converted to single crystal silicon ingot then analyzed by spectrophotometric methods to determine the trace impurities in them. Trace impurities in the polysilicon normally are acceptor (usually boron or aluminum, or both), donor (usually phosphorus or arsenic, or both), and carbon impurities [4].

2. POLYSILICON PRODUCTION OVERVIEW

The production of polysilicon requires several distillation process steps and more than 98% of electronic grade polysilicon is produced by the trichlorosilane ($SiHCl_3$) distillation method [2,5]. A summary of the processes involve is shown as follows.

2.1 **Sand to Metallurgical-grade Silicon**: High quality sand (SiO_2) is decomposed into metallurgical-grade silicon and carbon monoxide, according to the carbothermic reaction [6,7]:

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

(2.2) ***MGS to trichlorosilane:*** In order to reach a purity level suitable for semiconductor device applications, crude MGS will go through a purification step which involves the reaction of MGS with hydrogen chloride, HCl to form $SiHCl_3$. The following shows the main reaction of MGS with HCl to form $SiHCl_3$ [8].

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

2.3 ***Distillation of trichlorosilane:*** Liquefied trichlorosilane at room temperature is then purified by distillation process until the resulting impurity levels are at a few ppb. The impurities which remain in the purified $SiHCl_3$ are SiH_2Cl_2, $SiCl_4$, C, Fe, Ca, and Al [9].

2.4 ***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.

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

3. Polysilicon Growth in Chemical Vapour Deposition System

The polysilicon production scheme use in the actual polysilicon plant is illustrated in Figure 2. The plant produced its own HCl on-site using hydrogen, H_2 and chlorine, Cl_2. Hydrogen gas, H_2 is obtained via electrolysis of water and goes through a purification process normally by using palladium [10], platinum [11] or chrome nickel [12] filters. Figure 3 illustrates the overall process of producing pure hydrogen and finally HCl for polysilicon production. However, Cl_2 and MGS which are the starting raw materials are not produced on-site. HCl together with MGS are then processed in the TCS (trichlorosilane) plant to produce $SiHCl_3$ and $SiCl_4$.

Liquid $SiHCl_3$ which vaporizes at temperatures between 30°C to 32°C [8] is sent to a vaporizer where it will form $SiHCl_3$ gas by boiling liquid $SiHCl_3$ at temperature above 30°C. Both $SiHCl_3$ and H_2 gases are then directed into a chemical vapour deposition (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. 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. $SiCl_4$ is also widely used in the fabrication of fiber optics cable.

Figure 4 shows photo of the polysilicon rods in the CVD reactor which has been taken during the deposition process. Figure 5 shows the cross section of a CVD reactor showing the starting monosilicon seed. Polysilicon will deposit on the silicon seed and the duration of the process will depend on the required diameter of the rod. Similarly, in Figure 6 the cross section of the CVD reactor after the deposition process is shown here.

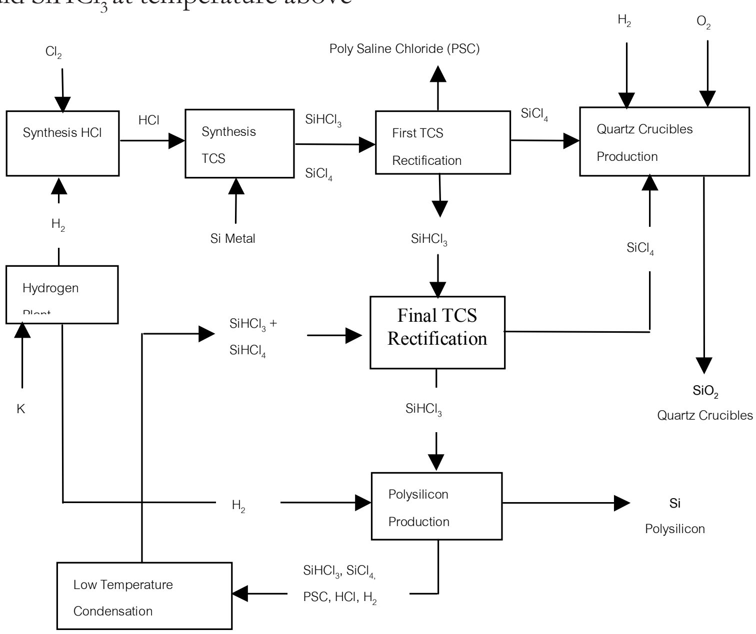

Figure 2. Polysilicon production scheme used in the plant.

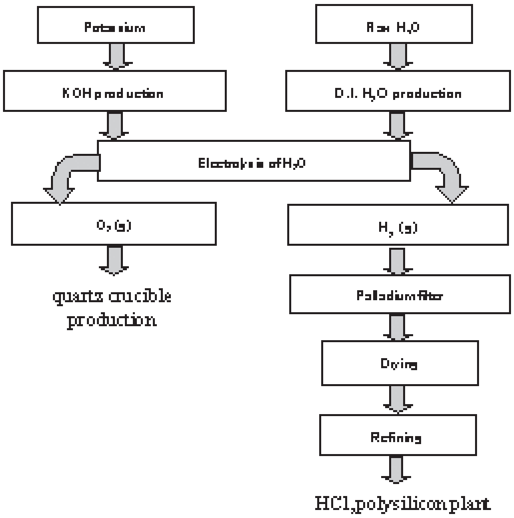

Figure 3. Hydrogen production process flow.

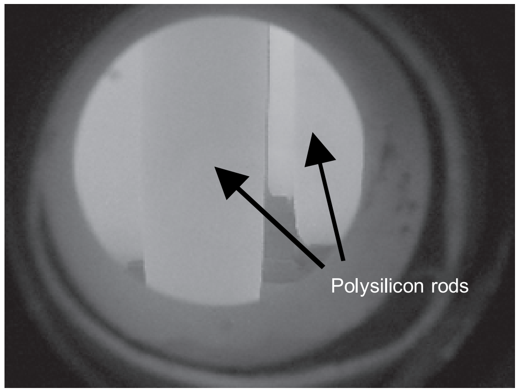

Figure 4. Photo of an actual polysilicon growth in the CVD reactor.

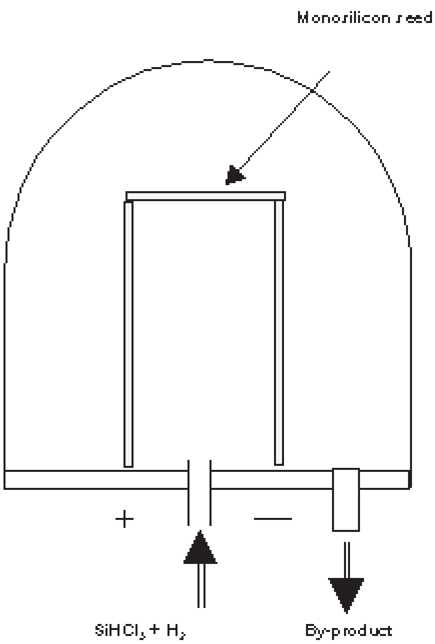

Figure 5. Cross section of the polysilicon CVD reactor before deposition.

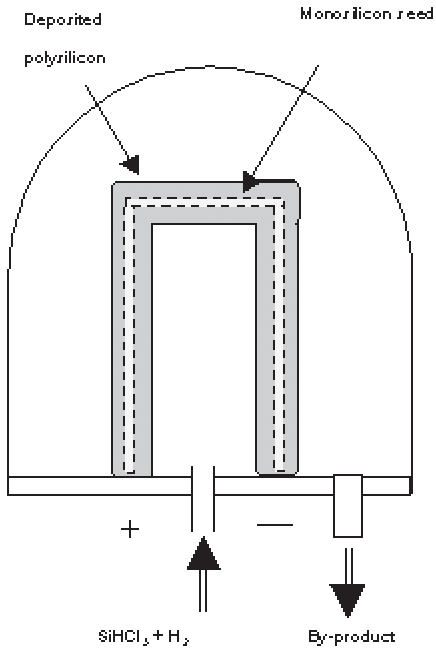

Figure 6. Cross section of the polysilicon CVD reactor after deposition.

Before the samples are taken out from the reactor, the CVD chamber will be cooled down. Figure 7 shows the polysilicon CVD reactors and while in Figure 8 shows polysilicon rods inside the opened chamber after deposition. Once the samples are removed from the chamber, they are cleaned using a mixture of hydrofluoric (HF) and nitric (HNO_3) acids.

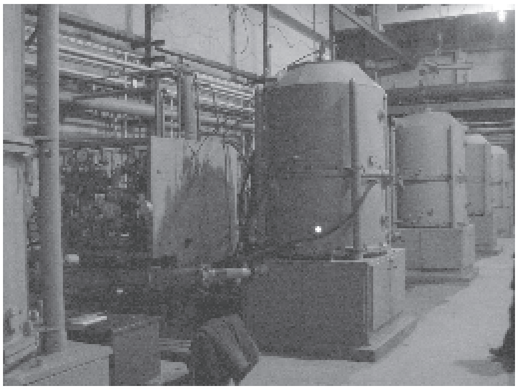

Figure 7. Polysilicon CVD reactors.

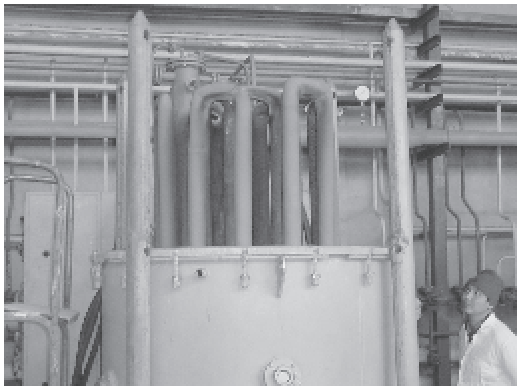

Figure 8. Polysilicon rods before unloading.

4. POLYSILICON CHARACTERIZATION

The evaluation of polysilicon is carried out using method as recommended by American Society for Testing and Materials (ASTM). Prior to characterization, the polysilicon are converted to monosilicon and finally analyzed using spectrophotometric technique to determine the trace impurities in them.

The ASTM F1723-96 (formerly known as F574) standard recommends the procedures for sampling polysilicon rods and growing monosilicon from the polysilicon samples by the Float-zone (FZ) method. The three main impurities tested as recommended are the donor, acceptor and carbon impurities. Additional test will be done for oxygen content, resistivity and carrier lifetime [13]. Table 1. shows the main impurities and standards used for analyzing them [13].

Table 1. ASTM Test Methods for polysilicon.

Parameter	ASTM Test Method	
III-V impurities (donor, acceptor)	F1630	Standard test method for low temperature FTIR analysis of single crystal silicon for III-V impurities
	F1389	Standard test method for photoluminescence analysis of single crystal silicon for III-V impurities
Carbon	F1391	Standard test method for substitutional carbon content of silicon by infrared absorption
Oxygen	F1188	Standard test method for interstitial atomic oxygen content of silicon by infrared absorption

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. The useful impurity range for oxygen is 0.01 ppm whereas the recommended value for resistivity is about 80,000 ohm-cm. In addition to the P, B and carbon impurities, several other impurities were also measured which includes iron (Fe), chromium (Cr), nickel (Ni), copper (Cu), zinc (Zn), and antimony (Sb). The polysilicon impurity test was done at Elkem in Norway and measured using Philips' PW2404 X-Ray Fluorescence (XRF) spectroscopy. Figure 11 shows the impurity components and respective level in the polysilicon sample as grown by the CVD. Recent development in analytical method has allowed the impurities to be measured in part per trillion levels using Inductively Coupled Plasma Mass Spectrometry or ICPMS. This technique is capable of measuring most of the elements in the periodic table [13].

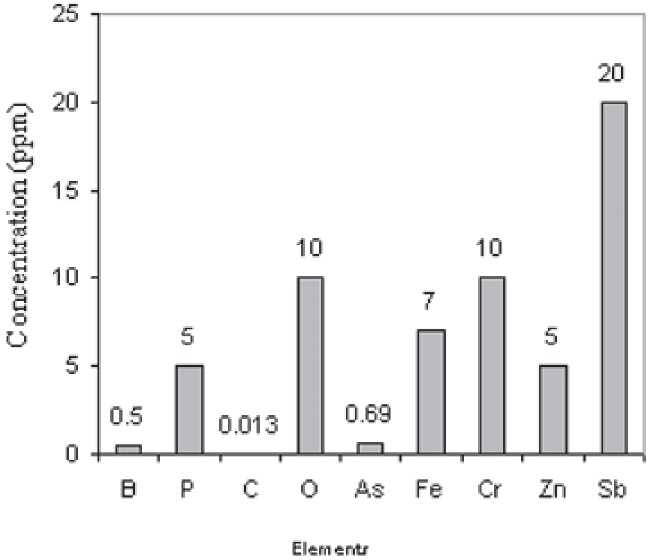

Figure 9. Impurity concentration in bulk polysilicon.

The impurity test results shows that B and P content are extremely high, above the recommended ASTM standard value. However, carbon content is still at an acceptable minimum value. Other impurities content such as As, O, Fe, Cr, Zn and Sb are still mainly above the maximum limit range.

The measured resistivity which is in the range of 30 to 40 ohm-cm shows that the polysilicon sample content high concentration of impurities in this case more towards n-type (phosphorus doped). Usually, the polysilicon samples are graded according to its purity level. A semiconductor or electronic grade polysilicon is 99.999999999% pure whereas a solar cell grade polysilicon is only 99.9999% pure. Based on the measurement of the impurity concentrations, the purity of the polysilicon is about 99.9995%.

Obviously, B and P content in polysilicon should be higher than standard value recommended by ASTM. On the other hand, other impurities have to be minimized also in order to improve the quality of the polysilicon grade.

5. Conclusion

The production of polysilicon has been carried out by the trichlorosilane distillation method grown inside a CVD reactor using the catalytic decomposition reaction of $SiHCl_3$ with H_2. Samples were sent to an independent test lab in Norway and tested using XRF spectroscopy. The test results shows that B and P content are extremely high, above the recommended ASTM standard value. Carbon content is still at a minimum level. Nevertheless, other impurities content such as As, O, Fe, Cr, Zn and Sb are also above the maximum values. The results shows that the purity of the polysilicon is only 99.9995% which is still below the requirement for a semiconductor grade polysilicon or a solar cell grade polysilicon. The measured resistivity in the range of 30 to 40 ohm-cm shows that the polysilicon sample contains high concentration of impurities which indicates the polysilicon is phosphorus doped.

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