Electrotechnology for Silicon Refining: Plasma Generator and Arc Furnace: Installations and Theoretical Base

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***Abstract*—**The photovoltaic and the semiconductor industries are in growth and it is necessary to supply a large amount of silicon to maintain this growth. Since silicon is still the best material for the manufacturing of solar cells and semiconductor components so the pure silicon like solar grade and semiconductor grade materials are demanded. There are two main routes for silicon production: metallurgical and chemical. In this article, we reviewed the electrotecnological installations and systems for semiconductor manufacturing. The main task is to design the installation which can produce SOG Silicon from river sand by one work unit.

***Keywords*—**Metallurgical grade silicon, solar grade silicon, impurity, refining, plasma.

I. Introduction

SILICON dioxide is a dielectric. This material is the most high-resistance dielectric which is used in microelectronics, compared with Al2O3, Si3N4. Silicon dioxide is the primary material for the production of high purity polysilicon. There are two main routes in the world for polysilicon production: chemical and metallurgical method. The most world common method for producing polysilicon is trichlorosilane process.

Metallurgical grade silicon (MG-Si) produced through the reduction of silicon oxide (quartz) with carbon in submerged arc furnaces. The process is characterized by large emissions of carbon monoxide. The main cascade of chemical reactions can be written as:

$$SiO_2 + 3C = SiC + 2CO \tag{1}$$

$$Si + SiO_2 = SiO \tag{2}$$

$$SiO + C = SiC + CO \tag{3}$$

$$SiO_2 + SiC = SiO + CO \tag{4}$$

$$SiO + SiC = Si + CO \tag{5}$$

The form for the process can be written as:

$$SiO_2 + 2C = Si + 2CO \tag{6}$$

The obtained MG-Si is not pure, usually 99.0-99.9% Si, and it contains a great number of impurities such as: Al, Fe, Ti, B, P, Mn, C and so on [1]. The minimum required purity of silicon for solar call applications is 6N- 99,9999% and for the semiconductor industry is 9N- 99,9999999%. The acceptable concentrations of each impurity in SOG-Si are determined by the conversion efficiency of solar cells. Traditionally, high pure SOG silicon has been produced through the well known Siemens process, which was developed in the 1950s. The production of silicon occurred by gasification of MG-Si, distillation and deposition of high pure silicon. Trichlorosilan (SiHCl3), TCS, is produced according to reaction (7) under high temperatures, typically at 500°C [1] and pressure near 30MPa [1]. The redistribution of chlorine and hydrogen atoms from SiHCl3 to SiH2Cl2 is then carried out by reaction (8). The produced dichlorosilane gas is distilled to monochlorosilane gas, which again is transformed to silane gas according to reactions (9) and (10). Through distillation, a lot of impurities are removed. This is an important step in the process, as the impurities effect on electrical characteristics of materials. The main cascade of chemical reactions:

$$5Si + 16HCl = 4HSiCl_3 + 6H_2 + SiCl_4 \tag{7}$$

$$2SiHCl_3 = SiH_2Cl_2 + SiCl_4 \tag{8}$$

$$2SiH_2Cl_2 = SiHCl_3 + SiH_3Cl \tag{9}$$

$$2SiH_3Cl = SiH_2Cl_2 + SiH_4 \tag{10}$$

The pure gas is decomposed to pure Si on a U-shaped filament according to reaction (11) [1] this chemical vapor deposition (CVD) reaction takes place at 1000-1100°C [1].

$$HSiCl_3 + H_2 = Si + 3HCl \tag{11}$$

The major problem of the chemical route is that it involves the production of chemical compounds and reactions with hydrochloric acid [1]. These compounds are very toxic and corrosive which causing irritations of the skin and mucous membranes. Chemical emissions in SOG silicon production by the chemical route are take place several times. These problems are solved by using electrotechnology, to produce SOG Silicon by reduction of river sand by plasma generator and electric arc.

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II. Silicon Refining by Plasma Generator

The advantage of induction heating is the high heating speed of materials and a wide range of temperatures. Temperature limited mainly only used materials. It allows obtaining a semiconductor with stable and homogeneous properties. Induction heating provides a high productivity and eliminate air pollution in most cases.

The primary task is to get tetravalent silicon powder 99.999% from river sand. This problem is solved by using the HFI-plasma generator with plasma gas - hydrogen [2]. For the plasma gas is used hydrogen, while the serial devices use argon. In the crystallization zone there is the set of traps to collect the low and high boiling impurities. Plasma generators (high frequency induction (HFI), unlike the widely used HFI discharges, for induction discharges transformer type coupling coefficient between the load (gas discharge), and the inductor (the primary winding of the transformer) is close to unit. At the head the plasma gas is supplied and plasma is produced using induction currents. The dosing material is river sand which fed from above, into the plasma, so the plasma temperature is controlled. The plasma generator decompose sand into the clusters (silicon and oxygen, separately). At the high temperature, the reverse reaction will not occur. After high temperature zone, the products of evaporation are rapidly cooled; preventing the reactions with oxygen and hydrogen and the hydrogen will have time to react with oxygen to produce water [2] in vapor form. Silicon oxide under the high temperature will vapor to silicon monoxide and silicon. The main cascade of reactions [3] occurring after the high temperature zone

$$SiO_2 + Si = 2SiO_{GAS} \tag{12}$$

$$SiO_2 + H_2 = SiO_{GAS} + H_2O \tag{13}$$

$$SiO_{GAS} + H_2 = Si + H_2O \tag{14}$$

$$H_2O = H - O - H \tag{15}$$

$$SiO_{GAS} + O_2 = SiO_2 \tag{16}$$

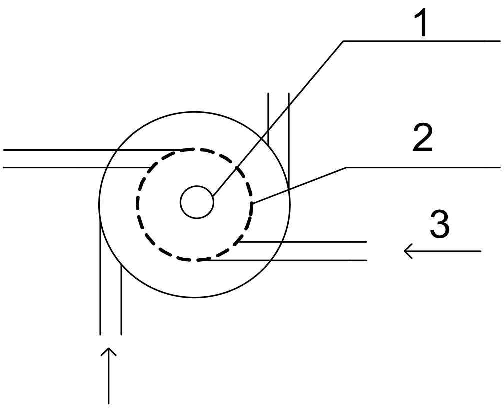

Fig. 1 High-frequency plasma torch

High-frequency plasma torch Fig. 1, includes: gas supply device 1, dose delivery system 2, an electromagnetic coil, inductor 3, plasma 4, thermal converter 5, thermal isolation 6. Plasma generator connected to a source of high-frequency energy, the discharge chamber and the plasma input unit.

Supply of material is carried out by vertically, to prevent contamination of the material and to increase the lifetime of the column the induction plasma gas is supplied tangentially 3.

Because of the tangential supply, heavy impurities concentrate near the edge of the column 2. Light impurities and raw material in the center of inductor 1.

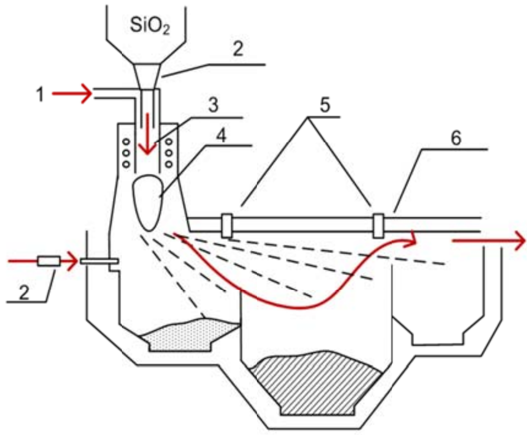

Fig. 2 High-frequency plasma torch with rows of the hoppers

Plasma gas is fed into the heating zone by tangential and heated by the vortical currents. Stabilization of the discharge in the arc plasma generator is achieved by magnetic field. Among the methods of gas stabilization, heat insulation and the compression of the arc is the so-called "spin". Gas is fed into the discharge chamber through the spiral channels, thereby forming a gas vortex, for the arc column and plasma jet is generated: a layer of cold gas under the influence of centrifugal forces is located near the chamber walls [4], preventing them from the contact with the arc. It is fair when a strong compression of the plasma flow is not required. Stabilizing gas often acts as a plasma-forming substance [5], [6]. Stabilization and compression of the arc by the stream of water is also applied. The three rows of collecting hoppers which are consists of an input unit 1, the collection hoppers 2, and filters 3. Silicon powder, after passing plasma generator, contains a large amount of light impurities and heavy metals. To refine this flow should be used three series of bunkers. Each row of bunkers designed for the most effectively collect certain element - silicon. Hoppers designed on base of: feed rate of the inert gas, the mass of the elements and the fall trajectory of the elements. In the first bunker will be collected heavy impurities. These impurities are served for secondary recrystallization for use it in the industry. The second tank must collect silicon nanopowder 99,99-99,999%. This powder is not acceptable for the semiconductor and photovoltaic industry. The use of this powder instead of metallurgical grade silicon 99% is not possible due to the high cost and complexity of high-volume production. Between the second and the third hopper is placed collecting filter for heavy impurities, i.e. impurities which weight is more than silicon. Heavy impurities are deposit in the third bunker. At the output of the third hopper installed cleaning filter for inert gas. Production cycle is closed, the inert gas is continuously moving in a closed circuit. The secondary use of the inert gas is acceptable due to the fact, that it does not lose its properties after passing through plasma torch. Power of plasma generator can reach 1 MW, frequency - from tens of kHz to tens of MHz, industrial efficiency 50-80%; operation resource is near 3000 hours [7].

III. Silicon Refining by Arc Furnace

The main purpose of this arc furnace is growing polycrystalline silicon. Arc furnace equipped with cleaning elements to obtain high quality silicon crystal. It allows removing light and heavy impurities that have a significant effect on the properties.

The heat transfer occurs in arc furnaces according to the law of radiation. The resulting heat stream between two surfaces is determinate by the law of Stefan-Boltzmann and Lambert. The form for this law is shown by (17)

$$Q_1 = C_1\left(\frac{T_1}{100} - \frac{T_2}{100}\right) \cdot F_1 \qquad (17)$$

where Q- heat stream, T- temperature, C- radiation constant, F- heated area.

The primary source of heat in the electric arc furnace is an electric arc which is burning between the electrode and the melt

The operating of the installation is carried out by feeding, from the top, the crude oxide of semiconductor (powder feed with the speed of 0.1-0.3 mm/min) on the molten semiconductor in a hydrogen atmosphere. Thus, obtained element, heated to the temperature above 3000 ^{o}C [8], [9]. Lifting machine shown on Fig. 2, consist of axle 1, electrode 2.

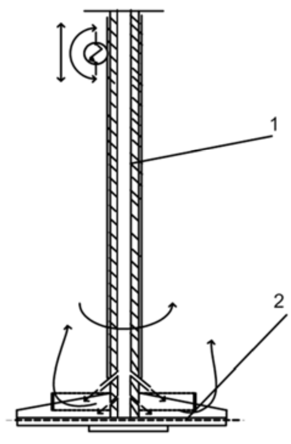

Fig. 3 Lifting machine

Simultaneously, the melt is agitated to facilitate the lifting of impurities due to the convection, form crust of the melt to surface. Adjustable voltage is supplied to the heaters through current conductor 2. On the surface of the melt occurred the main reactions [9]:

$$SiO_2 = SiO_{GAS} + 0.5O_2 \qquad (18)$$

$$SiO_2 = SiO_{GAS} + O \qquad (19)$$

$$SiO_2 = SiO + 0.5O_2 \qquad (20)$$

$$SiO_2 = SiO + 0.5O \qquad (21)$$

The crucible with the melt is shown on Fig. 4. The crucible is equipped with wheels 3 for loading and unloading of obtained silicon crystal. The inner part of the crucible has a conical form 2. At the bottom of the crucible 1 is loaded a small layer of high-purity silicon.

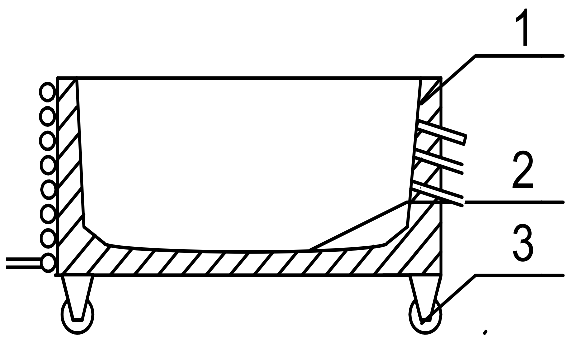

Fig. 4 Crucible

The semiconductor oxide reacts with hydrogen to form monoxide and water. The part of the impurities reacts with hydrogen and rise to the top. The exhaust gas with oxygen and impurities derived from the apparatus. Pure semiconductor remains on the surface of the melt Fig. 5.

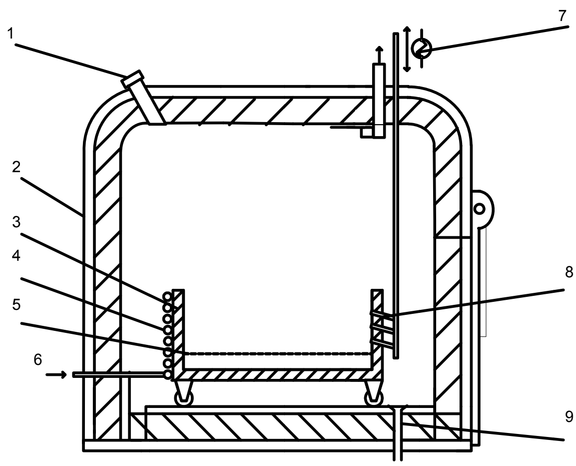

Fig. 5 Arc furnace crucible

Crucible 3 is cooled by circulated hydrogen 4 which is supplied throw the inlet aperture 6. Therefore, the crucible is heated not more than 50% of the melt temperature, which improves its service life and do not contaminate the melt. The heated hydrogen is then supplied to the feedstock hopper for preheating and partial purification. Formed on the surface of the melt layer of impurities 5 is drained through the drain holes 8 and removed from the reactor through the channel 9. After impurities removing, drain apertures are closing by aperture cap, which is moving by the drive 7. Melt solidification rate is equal to the head velocity of the heater, resulting the directional solidification of silicon, and further purify. The technological process is additionally monitored visually, through the window 1. The heat stored in the reactor by the heat insulator 2. Crucible moved by roller.

IV. Conclusions

Advantages of the offered method for solar grade silicon production from its oxide: high operation resource; all processes occurred in one unit; all reactions take place in the environment of hydrogen. Application of hydrogen is conditioned by that hydrogen does not contaminate the product of reaction [10], the market price of hydrogen is not high; all passing processes are ecologically clean. The hydrogen is clean by transport reactions and use again; it is possible to make fully automated process; construction of the unit allows using unrefined sand as a feedstock.

The main disadvantage is the complex protection unit. Protection block and automation systems must work in extreme conditions and ensure monitoring of all parameters continuously and with great precision, which ultimately affect on the quality of the manufactured products – silicon.

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