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INDUCTIVE PLASMA PROCESS FOR REFINING OF SOLAR GRADE SILICON

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Abstract

Refining metallurgical grade silicon to directly convert it into solar grade silicon appears to be one of the most promising ways to solve the problem of the silicon photovoltaic industry feedstock. Plasma refining consists in treating molten silicon with a reactive gas able to induce reactive volatilization of impurities. Oxygen, water and hydrogen chloride were tested as reactive gases from a theoretical and experimental point of view. Water, or a mixture of oxygen and hydrogen, is the most promising reacting gas in spite of the limitation by a silica layer at the surface of the liquid silicon.

1. Introduction

The PV industry which relies on crystalline silicon as feedstock material is facing a severe shortage of its classical silicon feedstock source: the wastes of the microelectronic industry. The strongly increasing demand induces a shortage of this feedstock, and the PV industry is now using electronic grade silicon, at the expense of the cost.

If metallurgical techniques applied on metallurgical grade silicon like segregation and directional solidification are able to significantly reduce the concentration of metallic impurities, it is not the case for impurities like Al, P, B, C, O, and Ca, the segregation coefficients of which are high. Impurities reactive volatilization can occur using plasma refining. The purification of metallurgical grade silicon by plasma has been studied by several research groups. The ENSCP group utilised an inductive argon plasma, in which oxygen was added as reactive gas. All the experiments were operated at low scale (less than 250 g). In the frame of the NEDO program, Japanese groups studied boron removal [1], and developed a purification process combining electron beam, arc plasma, and directional solidification. The electron beam was used to remove Phosphorus, the plasma treatment used water to remove Boron, and two directional solidification steps permitted to remove metallic impurities [2,3]. The amount of silicon treated during these studies reached 300 kg per batch. The process was able to produce solar grade silicon directly from metallurgical grade, but was not cost effective.

The present work deals with the design of a process taking into account the limitations of the previous studies. The expected difficulties were mainly due to the diffusion phenomena in the liquid bath. The impurities, that need to be volatilised, have to be transported to the surface of the liquid silicon bath, and the larger the size of the bath, the longer their diffusion time. The main idea was to use electromagnetic stirring of the liquid bath to overcome this problem. The use of an inductive cold crucible permits a very strong stirring. In the process developed, the electrical induction is utilised to heat the silicon bath, and the plasma to purify. Due to the plasma jet, the fast renewing of the gas within the boundary layer on the liquid surface was expected to ensure very low impurity concentrations in the gaseous phase and to facilitate the kinetic of purification. Moreover, when the reactive plasma purification is achieved, the controlled solidification in the cold crucible provides an important complementary segregation of the metallic impurities not volatilized during the plasma treatment, like iron and titanium. The continuous on-line monitoring of the flue gases was used to elucidate the purification mechanisms.

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2. Process

The pilot combines inductive plasma torch and inductive cold crucible in a chamber. The silicon to be treated was loaded inside the crucible, the capacity of which is 10 kg. The crucible is made of cooper and its bottom made of silica. During the process, owing to the electromagnetic repulsive forces, the liquid bath is free of contact with the crucible inner wall, and was supported only by the silica bottom. The plasma torch is made of three concentric tubes. The plasma gas is injected between the outer tube (i.d. 40mm) and the intermediate tube (o.d.38mm). The axial tube (o. d. 16mm), so called injector, is used for the injection of the reactive gas into the plasma. This axial injection permits to control the dispersion of the reactive gas inside the discharge. Indeed as shown in Fig.2, the recirculation vortex which remains inside the coil scatters the injected gas. That is why the tip of the injection probe is positioned after the vortex.

The plasma flow is laminar and consequently the diffusion of the injected gas is limited. The purification obtains a good efficiency regarding to the high concentration of the reactive gas close to the surface of the molten silicon. The plasma flow rate was 90 l/min, the intermediate flow 10 l/min, the injection flow 5 l/min, and the plasma power 25 kW. The plasma torch was positioned 4,5 cm above the cold crucible. The pressure inside the chamber was stabilised slightly above the atmospheric pressure (10^4 Pa) by the means of an automatic valve. The flue gases were sampled at the outlet of the chamber, and carried back to an analytical inductively coupled plasma (ICP) to be analysed by optical emission spectrometry (OES) [4]. It was then possible to analyse continuously the composition of the flue gases during the chemical treatment. The crucible induction frequency was 7 kHz, and the induction power 120 kW.

The process itself combines several stages. The first one is the start-up stage. Silicon is not a conductor at room temperature: it has to be melted by the plasma alone. Once the melting has begun, induction then takes over and insures the melting of the whole charge. The second step is the refilling: it is necessary to add silicon to the melted bath to fill the crucible when the initial load is melted. The third step is the chemical processing. The reactive gas was composed of a mixture of oxygen and hydrogen or of hydrogen chloride. The purification process is continuously controlled using the on-line analysis of the flue gases, monitoring the concentration of Carbon, Phosphorus, Boron and Silicon. The silicon concentration was used as reference, and the ratio B/Si has been used to determine the end of the process. The solidification was controlled by monitoring of the induction frequency, which vary with the amount of melted silicon.

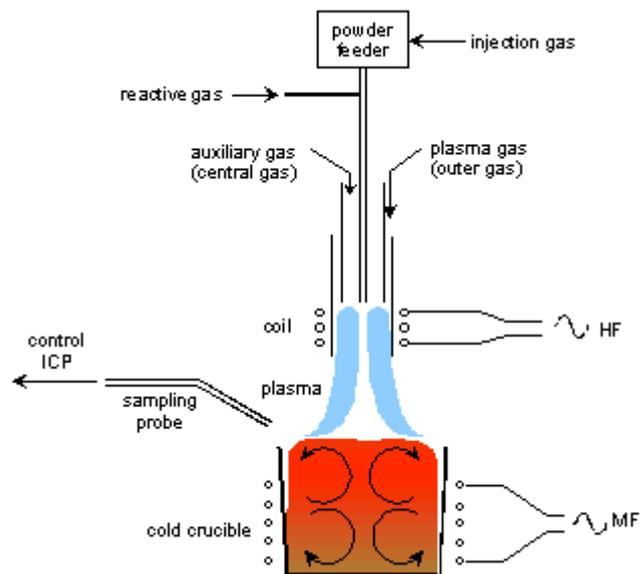


Fig. 1. Schematic diagram of the pilot.

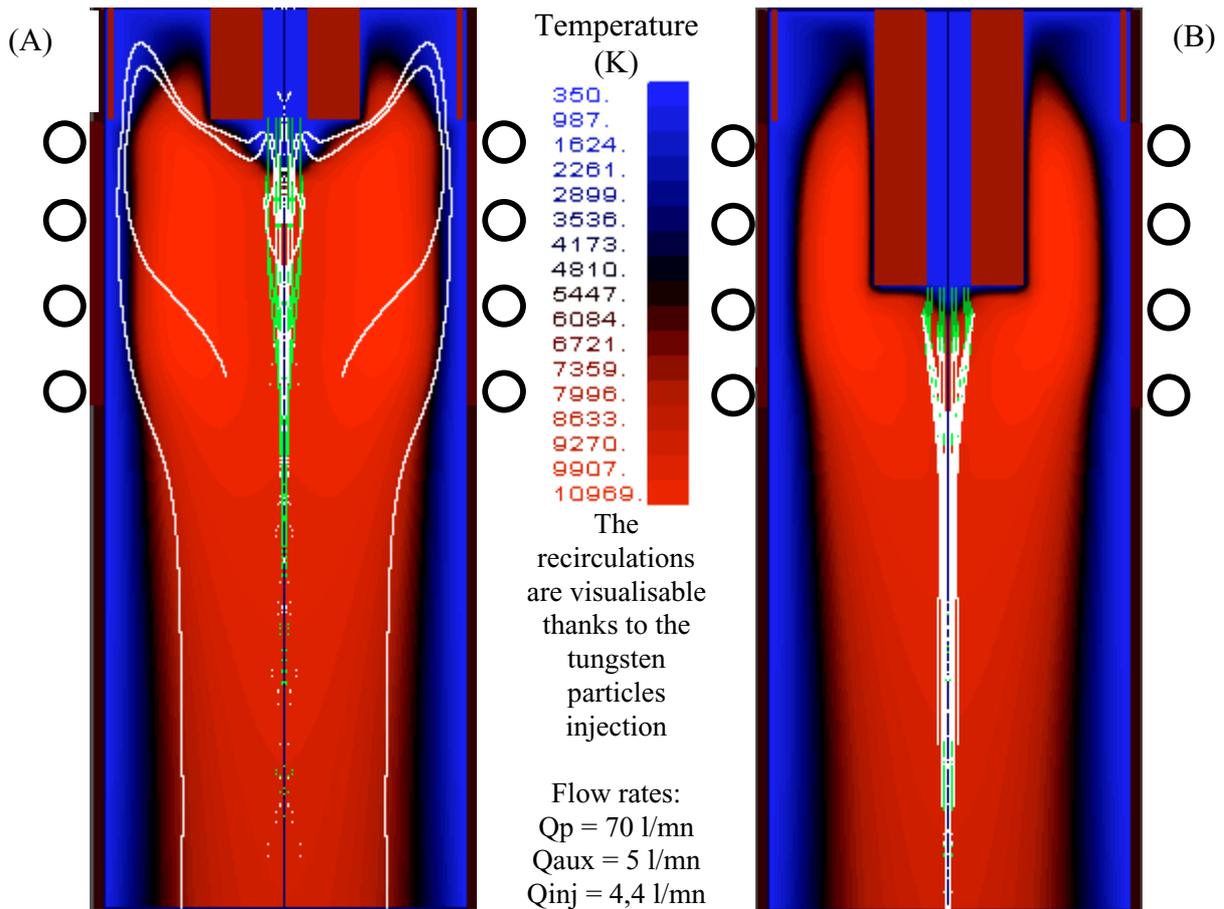


Fig. 2. Plasma torch simulation [5] of the temperature field with high (A) and low (B) injection probe position.

3. Thermodynamic study

Several reacting gases were investigated from a theoretical and experimental point of view: O_2 , H_2O , HCl and Cl_2 . The reason of this choice is due to a predictable limitation to the use of oxygen: the formation of a silica layer at high oxygen concentration, which limits strongly the purification kinetic. The goal of the thermodynamic study was to choose the reacting gas and the surface temperature for each purification gas. The principle of such calculation lies in the minimisation of the Gibbs free energy. The commercial code ADEP was used [6].

3.1 Oxygen and hydrogen

Boron is less volatile than silicon: its boiling temperature is 2820 K (silicon: 2540 K). It can be rendered volatile by simultaneous addition of oxygen and hydrogen: it will be evaporated under the forms of BHO (mainly), BO , and BH_2 (Fig. 3). At 1850 K BOH is ten times more volatile than BO : it appears that efficient boron removal requires not only oxygen, but also hydrogen or water. Carbon elimination requires either oxygen or water, and carbon will be eliminated as carbon monoxide.

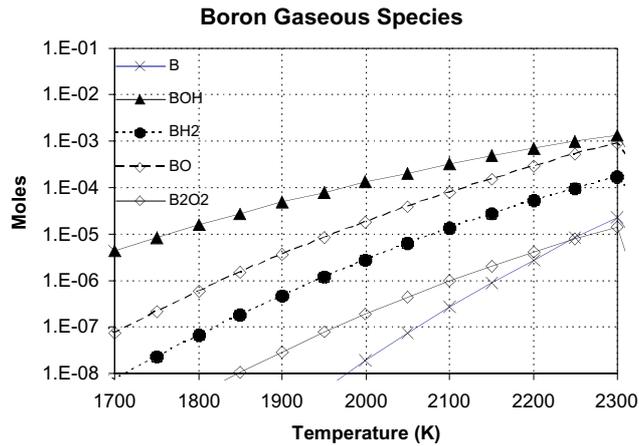


Fig. 3. Main boron gaseous species. Reacting gas: water. Initial concentration ratio B/Si : 10^{-4} .

From this study it has been possible to deduce the operating conditions required for each pollutant. The most difficult case seems to be Boron. Its removal requires high surface temperature and can cause important losses of silicon, through oxygen addition to the plasma. Hydrogen is required for efficient Boron removal.

During the silicon treatment with an oxygen-hydrogen plasma, the impurities volatilization is limited by the formation of a solid silica layer when the oxygen rate in plasma increases. For a concentration of O_2 in argon of 0,1%, we observe (Fig. 4) that the volatilization temperature ($SiO_2 + Si \rightarrow SiO$) of this layer is close to 1500K, whereas at 1% of oxygen this temperature is about 1650K, and is 1780K at 10% of oxygen, far above the melting temperature of silicon (1685K). The temperature of the liquid bath can be increased by increasing the induction power, as soon as the liquid bath has no more contact with the wall of the cold crucible, due to the Lorentz forces. On the other hand, decreasing the distance between the plasma torch and the liquid results in an increase of the heat transfer to the surface.

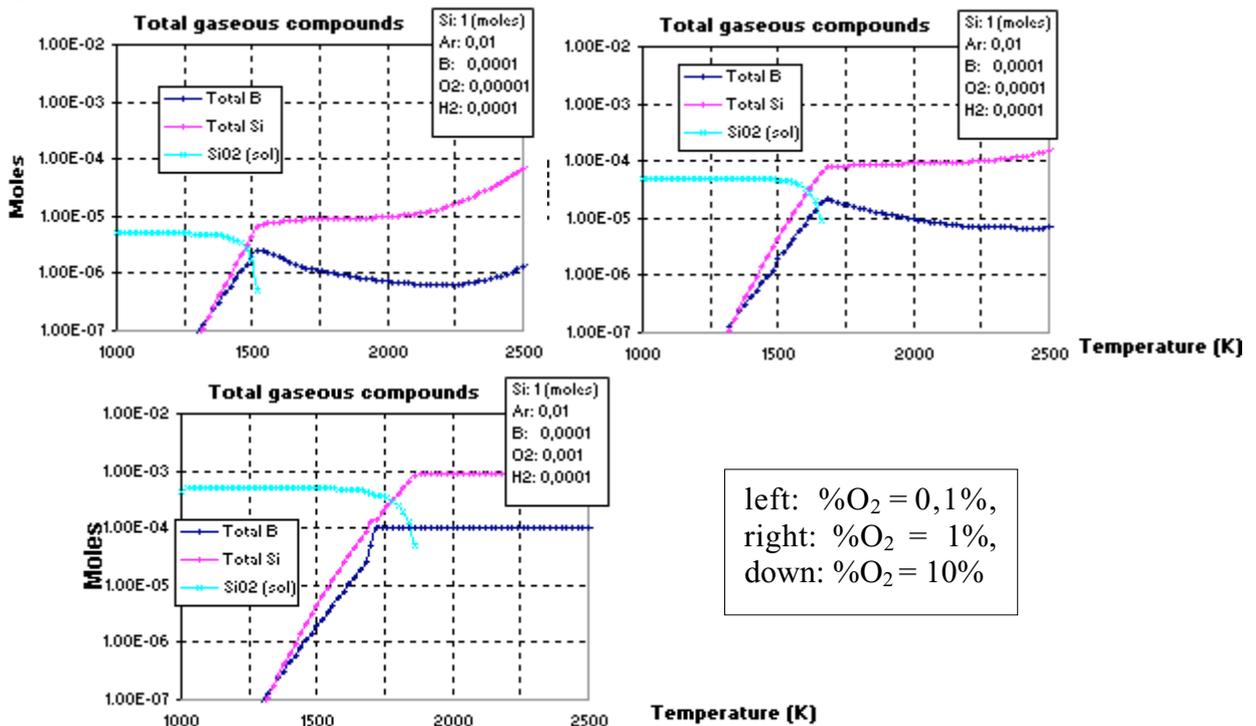


Fig. 4. Results of reaction simulation of oxygen and hydrogen ($\%H_2 = 1\%$) with 100ppma boron.

3.2 Hydrogen chloride

The investigation of chlorine and hydrogen chloride as reacting gas is of interest because there is no solid reaction product with silicon. Consequently we can hope to be able to operate at high reacting gas concentration and thus to speed up the purification process. We have preferred hydrogen chloride because it is easier to neutralize. The thermodynamic calculations show that it is possible to obtain volatile compounds. As shown in Fig.4, boron would be volatilized into the main volatile species BCl_2H , BCl , BCl_2 , BClO , ...

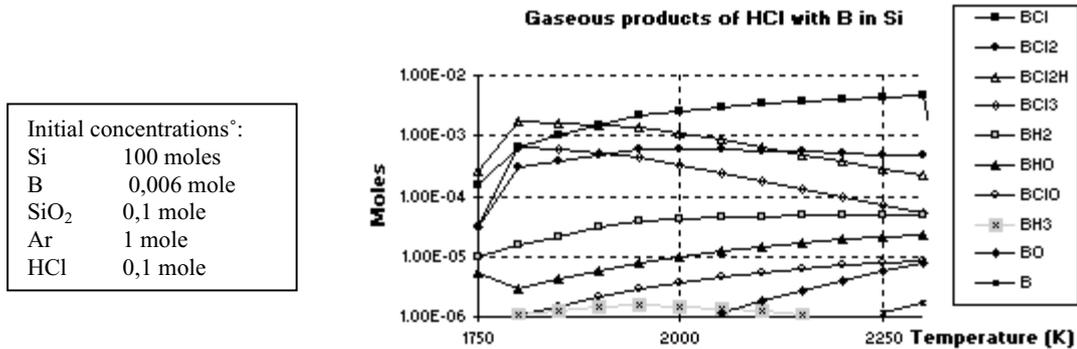


Fig. 4. Boron volatilization.

4. Experimental study

4.1 Oxygen treatment

The silicon powder was provided by RIMA (Brazil). The typical composition of this material is given in Table 1. When the reacting gas is only oxygen, the ratio B/Si is roughly 8 times lower than with a mixture of 50 % in oxygen, 50 % in hydrogen. The boron volatilization rate depends directly on the oxygen flow until hydrogen is in excess. These observations are coherent with the predictions of the thermodynamic calculations, and confirm that boron is mainly eliminated as BOH. When the oxygen flow rate overruns 0.4 l/min, the boron and silicon concentrations in flue gases drop dramatically. Simultaneously one can observe the formation of a thin white layer of silicon dioxide at the surface of the bath. At low oxygen flow rate silicon is oxidised under the form of silicon monoxide, SiO , which is gaseous at the silicon melting temperature. At high oxygen flow, the formation of a thin solid skin at the surface of the bath limits dramatically the chemical exchanges with the plasma. The evolution of the boron concentration in the flue gases during the chemical treatment has been recorded over a long period, running at constant oxygen and hydrogen flow rate. Fig. 5 shows this evolution, suggesting a first order kinetic. The rate constant is very close to those determined by the Kawasaki group [2].

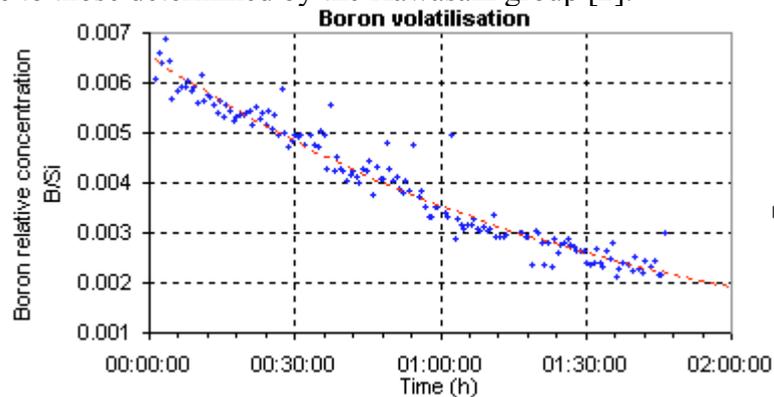


Fig. 5. Evolution of B/Si ratio in flue gases during plasma treatment.

Silicon obtained by oxygen / hydrogen treatment made it possible to produce solar cells with 12,4% of efficiency [8].

4.1 Hydrogen Chloride treatment

In a second step HCl has been used as reacting gas. The plasma flow rate was 83 l/min, the intermediate flow 4,5 l/min, the injection flow 2,7 l/min. The HCl flow rate varied from 0,5 to 2,5 l/min. The volatilization of silicon was dramatically increased, but the volatilization of boron was only weekly increased and the B/Si ratio remained around 10^{-5} . The silicon losses during the treatment were very important. This departure from the thermodynamic calculations are surprising: with the oxygen treatment we observed a good agreement between theoretical and experimental results.

This fact could be due to the formation of silicon borides SiB_x ($x = 3,4,6, \dots$), which are stable up to 2100K (Fig. 6). The energy of the B-O bond is higher than those of the B-Cl bond, and the oxygen treatment is probably able to dissociate the borides, contrary to HCl.

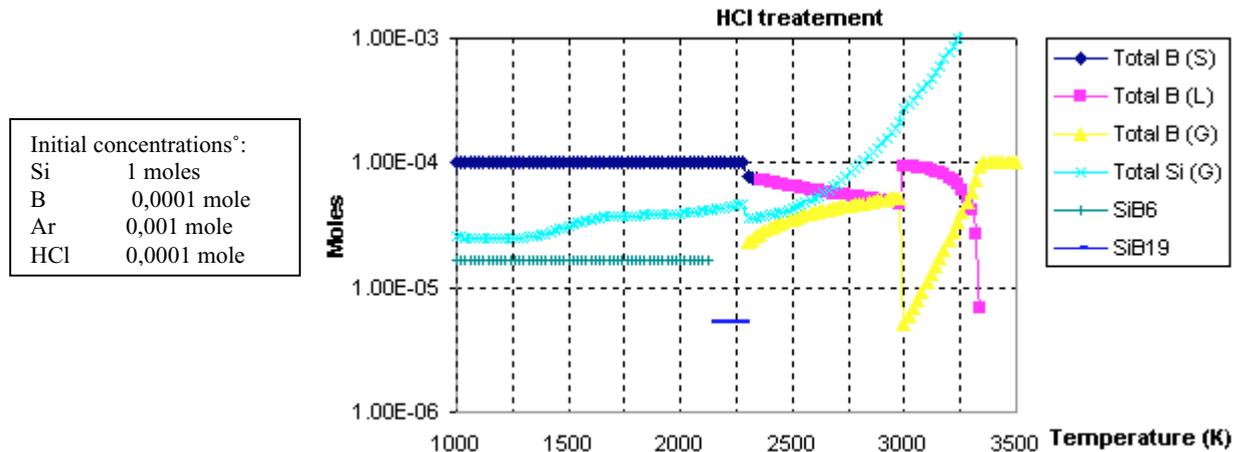


Fig. 6. Formation of silicon borides.

5. Conclusion

Combining electromagnetic heating and stirring with inductive plasma permits to purify upgraded metallurgical silicon at reasonable cost. The electromagnetic stirring speeds up the diffusion of the impurities to the surface and the inductive heating allows to reduce the plasma power. Boron volatilization requires a mixture of oxygen and hydrogen, or water. Among several reacting gases like water, oxygen, hydrogen chloride or chlorine, the mixture water or oxygen and hydrogen remains the most promising in spite of the disadvantage linked to the silica layer formation. Some further improvements of this process could be make it cost effective, and reduce the total treatment time.

References

- [1] T. Ikeda, M. Maeda, ISIJ International 32 (1992) 635
- [2] N. Yuge, H. Baba, Y. Sakaguchi, K. Nishikawa, H. Terashima, F. Aratami, Solar Energy Materials and Solar Cells 34 (1994) 243.
- [3] Y Sakaguchi, N Yuge, N Nakamura, H Baba, K Hanazawa, M Abe, Y Kato, 14th European Photovoltaic Solar Energy Conference, Barcelona (1997) 157.
- [4] C. Alemany, C. Trassy, Progress in Plasma Processing of Materials 2001. (in the press).
- [5] P. Proulx, J. Mostaghimi, M.I. Boulou, Plasma Chemistry and plasma processing, 7 (1987), 29-53.
- [6] ADEP, SPCTS, Limoges University, 87060 Limoges cedex, France.
- [7] Binary Alloy Phase Diagrams (1986), ed. T.B. Massalki, J.L. Murray, L.H. Bennett, H. Baker, publ. American Society of Metals
- [8] R. Einhaus, D. Sarti, C. H sselser, C. Trassy, Y. Delannoy, S. De Wolf, F. Ferrazza, S. Martinuzzi, W. Warta. IEE Conference on Photovoltaic Applications, Anchorage, USA (September 2000) 221-224. ISSN 1290-8371