Rapid Communication

Development of silicon purification by strong radiation catalysis method

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Using a new type of solar furnace and a specially designed induction furnace, cost effective and highly efficient purification of metallurgical silicon into solar grade silicon can be achieved. It is realized by a new method for extracting boron from silicon with the aid of photo-chemical effect. In this article, we discussed the postulated principle of strong radiation catalysis and the recent development in practice. Starting from ordinary metallurgical silicon, we achieved a purification result of 0.12 ppmw to 0.3 ppmw of boron impurity in silicon by only single pass of a low cost and simple process, the major obstacle to make 'cheap' solar grade silicon feedstock in industry is thus removed.

Keywords: silicon purification, strong radiation catalysis, boron removal, solar furnace
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1. Introduction

In a previous article,[1] we have reported a new type of solar furnace as a strong radiation means to be used to purify metallurgical silicon into solar grade silicon. Following the same line, we have made much progress in terms of quality and quantity of the purified silicon using this method. Some pilot scale project has been made and the removal effect of boron has dramatically improved from the previous 1 ppmw (1 ppmw=10^{-6} in weight) level to less than 0.3 ppmw level. Meanwhile, in the study of the principle of purification, we found that not only radiation from the Sun can be utilized for induced photo-catalysis, but also laboratory-made strong radiation like the space-compacted high-temperature induction furnace with black body temperature of 2200 K or higher can also serve the same purpose, although the reaction speed is reduced accordingly in comparison with the photo-catalysis from the Sun where the black body temperature is 5777 K.

2. Preliminary study of the principle of strong radiation catalysis

In our previous experiment,[1] it was discovered that the reaction rate of removing boron from silicon is hundreds or thousands times faster than that in the conventional slagging method.[2] As we know, reasonable removal of boron from liquid silicon needs a few hours to complete while in the solar furnace, only less than one second is enough. The huge reaction speed difference cannot be fully explained by other factors such as the differences of the contact surface, masses, the processing temperature, etc. We thus presume that there must be some kind of catalysis existing in the chemical reaction processes. Ho, Qing and Chen[1)] thought that the photon-catalysis functioning in ordinary temperature and weak radiation circumstance could also take effect in high temperature and strong radiation circumstance. They postulated an Arrhenius–Ho high temperature photo-chemistry formula to evaluate the reaction rate as follows:

[1)] Ho T H, Qing C R and Chen Y T "A new discovered quasi-stabilized chemical reaction system in macro scale ", *Celebration of Prof. Zhou GuangZhao' s Achievement in Theoretical Physics for the Past 55 years*, 2010.

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$$k = aT^m \mathrm{e}^{-(E_\mathrm{a}-E_\mathrm{p})/RT}, \quad (1)$$

where a, m are the constants to be determined by experiment, T is the reaction temperature, R is the Avogadro constant, E_a is the activation energy, E_p is the photon energy function related to the photon flux and the average energy of the photon. Indeed we should also know the detailed form of the function of E_p. But we know that if two processes having the similar value of photon flux and the average energy of photon, the reaction rate should be close at the same reaction temperature. Therefore, let us estimate the values of the two parameters in a new type of solar furnace and induction furnace, which can also be used in the laboratory to produce strong radiation. For a 10000 times concentration of solar ray, if the one Sun's flux on the surface of the Earth is 1000 W/m^2, the calculation shows that the photon flux can reach 0.4×10^{22}/cm^2·s with average photon energy of 1.34 eV from a black body (5777 K) radiation.

Then, the average photon energy from a black body of 2200 K can be estimated as

$$1.34 \text{ eV} \times \frac{2200}{5777} = 0.51 \text{ eV}.$$

The photon flux, according to Stefan's law, should be

$$\frac{\sigma T^4}{0.51 \text{ eV}},$$

where σ is the Stefan's constant. The result of the above formulae is 1.61935×10^{21}/cm^2·s. It is in the order similar to that obtained from solar energy concentrated by new type of solar furnace. Although the average photon energy in induction furnace is much less than that of solar furnace, the similar order of flux has indicated the existence of photo-effect in the furnace. It is inevitable that the reaction rate would be slower than that in solar furnace; the employment of a crucible would allow a longer reaction time.

3. The principle to realize the strong radiation in practice

3.1. New type of solar furnace

From a series of research works by Chen *et al.*,[3−6] a new type of solar furnace has been realized by using a non-imaging focusing heliostat operating in the spinning–elevation Sun tracking mode and equipped with a line-tilting mechanism for the elimination of off-axis aberration to the first order. A non-imaging focusing heliostat is a two-axis Sun tracker consisted of a mirror array in which the mirrors are tilted by group along only row and column directions. It is found that in optics, in order to use the line movement to eliminate the optical aberration, the only tracking mode is the spinning–elevation mode.[7] The spinning axis points towards a target while the elevation axis is perpendicular to the spinning axis. The movements of both the axes are given by the spinning angle ρ and the elevation angle θ as follows:

$$\theta = \frac{\pi}{4} - \frac{1}{2}\arcsin\{-\cos\delta\cos\omega\,(\sin\lambda\cos\Phi + \cos\lambda\cos\phi\sin\Phi) - \cos\delta\sin\omega\cos\lambda\sin\phi + \sin\delta\,(\cos\lambda\cos\phi\cos\Phi - \sin\Phi\sin\lambda)\}, \quad (2)$$

$$\rho = \arcsin\left\{\frac{-\cos\delta\cos\omega\sin\phi\sin\Phi + \cos\delta\sin\omega\cos\phi + \sin\delta\sin\phi\cos\Phi}{\cos\beta}\right\}, \quad (3)$$

$$\beta = \arcsin\{-\cos\delta\cos\omega(\sin\lambda\cos\Phi + \cos\lambda\cos\phi\sin\Phi) - \cos\delta\sin\omega\cos\lambda\sin\phi + \sin\delta\,(\cos\lambda\cos\phi\cos\Phi - \sin\Phi\sin\lambda)\}, \quad (4)$$

where ω is the hour angle of the Earth, φ is the facing angle of the heliostat, λ is the target angle of the heliostat, Φ is the latitude of the location of the heliostat, δ is the declination angle of the Sun.

The following illustration gives a better explanation of the parameters mentioned above.

Figure 1 shows the orientation of heliostat axes operating in the spinning–elevation tracking mode and the definitions of the parameters used in the spinning–elevation tracking formulae. In the diagram heliostat frame is not shown.

The tilting of the mirrors along row and column directions can be calculated by the following formulae

$$\sigma = \frac{1}{2}\arctan\left(\frac{H\cos\theta}{H\sin\theta + L}\right), \quad (5)$$

$$\gamma = \frac{1}{2}\arctan\left(\frac{H}{L\cos\theta}\right), \quad (6)$$

where H is the vertical distance of the centre of facet mirror to the centre of the mirror array, L is the distance between the target and the centre mirror of the heliostat.

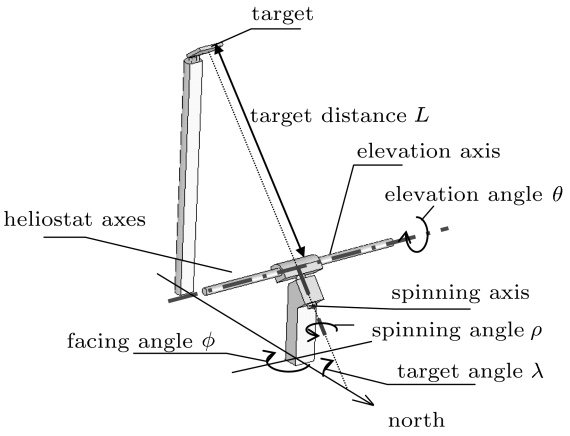


Fig. 1. The schematic diagram of the new type of solar furnace.

The two axes, spinning axis and elevation axis, are tracked automatically with solar time to realize group tracking, an active control of the shape of the mirror array is realized by the row and column tilting to reduce the optical aberration, which is otherwise intrinsically existed in classical optics. The active optics here provides a low cost and highly efficient concentration for heliostat. With the above group and slave tracking, it is a fairly easy job in the experiment to reach a concentration of 10000 times or more to meet the strong radiation condition. On the surface of the Earth, the photon flux received from the Sun is $0.4\times10^{18}/\mathrm{cm}^2\cdot\mathrm{s}$, therefore, for a concentration of 10000, the flux may reach $0.4\times10^{22}/\mathrm{cm}^2\cdot\mathrm{s}$.

We may see that, for a reasonable reaction rate, any laboratory-made apparatus to serve the same purpose should have the similar order of the optical flux.

3.2. Induction catalysis furnace

However, solar furnace method suffers from an important shortcoming: it simply cannot work when there is no sunshine. This shortcoming hindered the development of strong radiation catalysis method in many areas where the solar resources are not sufficient. For the wide use of radiation catalysis in industry, we need to explore an method by using different furnaces, particularly the induction furnace to replace solar furnace as a natural compensation in many circumstances. Induction furnace with a graphite crucible may reach high black body's temperature and within a small space, the radiation can be considered as strong radiation comparable to the Sun's radiation. The detailed design will be illustrated in the following section.

4. Experimental setups

According to the above discussion, there are two kinds of furnaces, i.e., new type of solar furnace and induction furnace. The experimental setups are illustrated in Figs. 2 and 3 respectively.

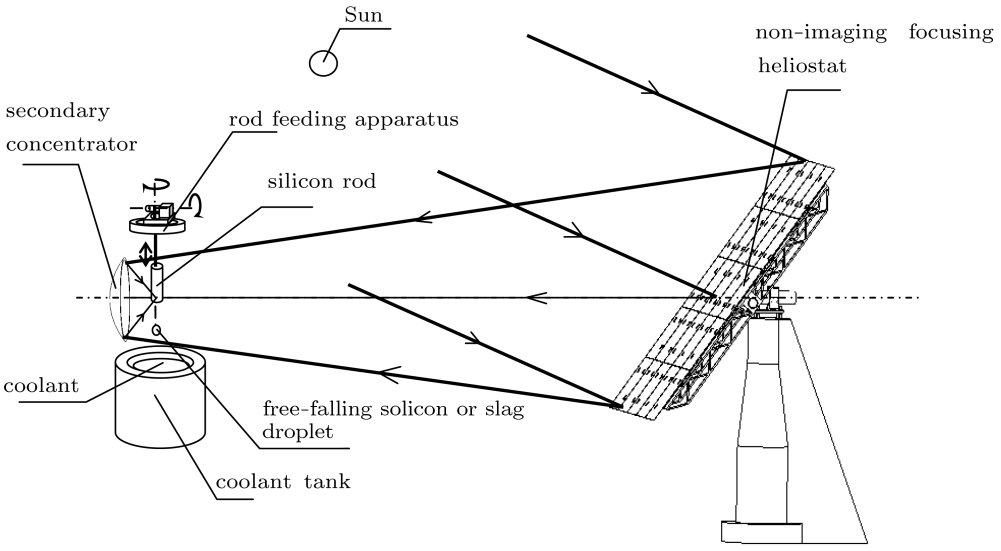


Fig. 2. The experimental setup of silicon purification using a new type of furnace.

In Fig. 2, a mirror array of 8 m×8 m in square consisted of 289 pieces of facet mirror acts as a non-imaging heliostat. The group tracking is performed by using spinning–elevation tracking formulae as shown in Eqs. (2) and (3). Slave tracking is performed by row and column movements according to Eqs. (5) and (6). Solar ray with more than 100 times of concentration incidents on a very small secondary concentrator to obtain a final concentration of 10000 times. The strong radiation is incident on a rod of mixed silicon and metal oxides to have instant melting and chemical reactions. The molten mixture thus drops by gravity free-falling into the cooling liquid to separate silicon and residual slag.

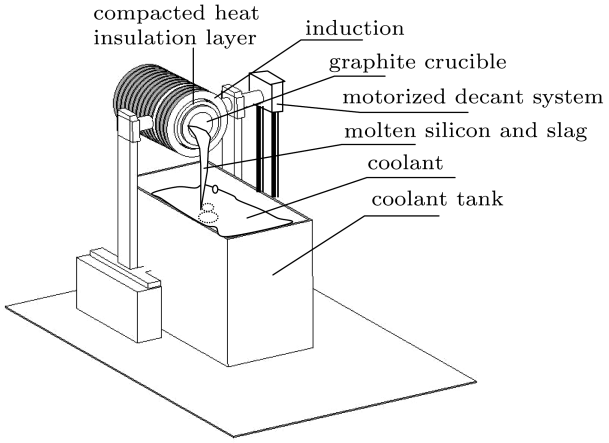


Fig. 3. The experimental setup of silicon purification using an induction furnace.

In Fig. 3, a high quality graphite crucible is powered by induction coil. Between the coil and crucible, a special material of isolation layer is designed to have thermal isolation function and act as radiation reflector. The isolation layer and the crucible are so designed that they are forming a compact optical cavity to create a strong radiation when electrical current pass through the coil. For a typical design, the optical cavity has a diameter of 400 mm and a height of 450 mm. Powered with 150 kW, the strong radiation thus produced can reach optical flux of $1.6\times10^{21}/\mathrm{cm}^2\cdot\mathrm{s}$ to match that in the solar process.

5. Major improvement comparing to the previous experiment

In both of the experiments, we improved the previous work reported in 2009 mainly in the reaction temperature. As we reported earlier that the reaction temperature was determined by the phase change point, which is in turn adjusted by the composition of the metal oxides added to the mixture of the silicon rod. As discussed in Section 2, the photon flux, which can affect the reaction rate is proportional to the 4th order of the temperature; the authors thus guess that the reaction temperature must be very sensitive to the speed of the reaction. Therefore, in the present experimental setups, the metal oxides addictives should be so chosen that the phase change temperature maintaining at the point that must be as high as possible in practice. Although only in terms of the melting points of the metal oxides, the phase changing temperature may reach 2600 K or higher. This is impractical for a normal process. Very high reaction temperature can lead to great loss of silicon due to liquid silicon's vaporization. The silicon loss can be reasonably controlled in solar furnace because the process time is relatively short, in the order of second; the loss becomes much greater in the induction furnace because the process time is much longer than that in solar process. For example, in an experiment, we once tried 2400 K for the reaction temperature and resulted in only 20% of silicon left. In the induction furnace, if the operation temperature is over 2200 K, many technical obstacles occur; among them, are water cooling problem, isolation layer's problem, the problem related to the quality of graphite, etc. A sufficiently high operation temperature is rather critical in our experiments. According to Fig. 2, the molten materials will drop upon melting in a crucibleless operation mode, thus the exposure time to the radiation is only limited to less than one second. Because of that, purification reaction must be completed within this period, otherwise, the purification results would not be satisfactory. While in induction furnace, any prolonged reaction time will lead to serious loss of the silicon. For the above-mentioned complication, this improvement is not so easy to be accomplished. The reason is obvious. The metal oxides added in the silicon rod have two roles: to participate the chemical reaction to remove the impurity and at the same time to adjust the euthetic temperature of the mixture. Great efforts are paid to optimize the working condition to meet both of these requirements. After many experimental trials, finally we found out that 2200 K is the most suitable reaction temperature and at this temperature the resulted silicon from certain processing mixture of raw silicon and metal oxides may obtain the best purification result within the shortest time.

In designing of the induction furnace, one factor

limits the size of the crucible, the melting speed. According to the above illustration, there are three steps in the process, heating, melting and maintaining the reaction. The maintain time, i.e., the time period between the melting and decanting down, is critical for the final result of the process. If it is too short, the reaction cannot be completed, if it is too long, the silicon loss could be too much due to high temperature vaporization. Therefore, it is required that the melting situation of the materials inside the crucible is reasonably homogeneous in space. Of course, the larger of the size of the crucible, the longer it takes for the total melting and the worse for the homogeneity to be destroyed. On the other hand, for any industrial usage, we would hope the size of the crucible to be designed as large as possible. At present, in practice, the biggest furnace to meet both of the above conditions is with a size containing 25 kg raw material and equipped with power supply of 150 kW.

6. Present purification result

With the strong radiation catalysis effect discussed above using the solar furnace or induction furnace, we can remove the impurities of the elements in IIIA group of the periodic table particularly boron with high efficiency. Table 1 lists some of the typical results obtained in recent experiment.

Table 1. Typical result for the removal of impurities by strong radiation catalysis. (1 ppm=10^{-6})

impurity	boron	aluminum
before refinement	3.5 ppm	86 ppm
after refinement	0.12–0.3 ppm	0.1–0.6 ppm

As we know that usually we define a parameter,

$$\alpha = \frac{\text{Boron concentration before purification}}{\text{Boron concentration after purification}}$$

as an evaluation parameter for the efficiency to remove boron impurity for a particular method. However, the value of α is usually 2–5 for ordinary slagging method[9] for a single pass of the slagging process. In our case, the value of α has reached more than 10 is a rather special achievement. In fact, some of the values of α are above 30, resulting in boron concentration as low as 0.12 ppm for one pass of processing.

Although the above two methods may reach nearly the same result, their performance is different.

7. Performance report of two methods to produce strong radiation

These two kinds of furnaces, solar and electrical induction, according to the above illustration may produce nearly the same order of radiation flux in the experimental area, have some differences. These differences may lead to different designing in industrial production lines.

7.1. Electricity consumption

As we know, solar furnace is to concentrate the solar ray as strong radiation power, the electricity consumption is only restricted by the tracking of heliostat, water cooling and other auxiliary's usages. The experiments show, that total electricity consumption is less than 2 kW·h per kg of silicon produced. In the case of induction furnace, considerable electricity is required for the operation, including the heating, melting and maintaining for reaction. In the earlier work, we found that due to the requirement of longer period for maintaining the chemical reaction process, the major portion of the electricity consuming was used in this stage and the total consuming of electricity was in the range of 50 kW·h/kg–70 kW·h/kg. However, after the proper applying the radiation catalysis, the maintaining period of reaction process has shortened from about 1 h to 5 min. With this catalysis effect, the experiments show that the total electricity consumption is 20 kW·h/kg.

7.2. Contamination during the refining process

As shown in Fig. 2, in the solar furnace refining process, the raw silicon rod is processed under a crucibleless condition with a non-contact manner. The resulted molten silicon drops are free-fell in to a liquid for a quick cooling. The liquid is clean at least in terms of the residual elements of Al, B, etc. All these measures have limited the possible contamination, particularly the contaminations by the crucible surface contact due to direct diffusion or solution at high temperature.

Many efforts have been made to use the same manner in the induction furnace but failed. As shown in Fig. 3, a graphite crucible has to be used for two functions: as an induction heater and as a container.

Contacting graphite at high temperature may cause many contaminations. The following table gives some typical value in the experiments:

Table 2. Typical contamination in the induction furnace by graphite crucible.

impurity	Phosphorous	Iron
before refinement	7 ppm	80 ppm
after refinement	13 ppm	200 ppm

Another serious contamination element is carbon as we can imagine that the impurity comes directly from the crucible itself. The extent is naturally depending upon the quality of the graphite material used. We have not examined this contamination by experiment carefully, but the observation of existence of silicon carbide in some batches of processed silicon gives the evidence.

Although it is indeed that the induction method will cause secondary contamination, this sacrificing has exchanged by the effective removing considerable amount of boron which is the most difficult element to extract from silicon. The newly added impurities will be removed by other conventional methods.

From the above performance report, we can anticipate that using the furnace to produce strong radiation for the purification of silicon may well be applied in the solar grade silicon in large industrial scale but the prospect to have a further purification for the use of semiconductor grade is faint. On the other hand, solar process introduces nearly nil contamination, with a reasonable yielding rate (see the report of the next section), multi-pass process may produce silicon containing boron of less than 10^{-9}, opening a new way to produce electronic grade of silicon in future.

7.3. The yielding rate

The high temperature reaction condition will inevitably cause the silicon loss due to vaporization, oxidization and other mechanisms. To reduce the loss, the key issue is to shorten the reaction time while to ensure the reaction process to be sufficient and thorough. The reaction time in solar process is determined by the nature of crucibless character and the reaction time of the inductive process can be determined by balancing all factors. As we mentioned before, for a large furnace with electrical power of 150 kW, the optimized time is about 5 minutes. Therefore, generally speaking, the yielding rate in solar process is higher than the process using induction furnace. Experiments show that 80% yielding has been reached for the first type of process, while 60% yielding has been reached for the second type of process.

7.4. The production rate

The nature of solar furnace has determined that a continuing production is impossible. Experiments show that with a cloudless weather and Sun flux greater than 700 W/m^2, the production rate for one unit of furnace, the furnace we illustrated in the experimental setups, is 0.7 kg/h. This figure may be further improved in the future by altering many of the furnace's designing. The discontinuing character of the solar process is the major disadvantage. The interesting point is that the most troublesome phenomenon in the discontinuity is not the long term interruption of the sunshine such as day and night, raining and shining, it is the short term shifting of cloud and shine. This short term weather change will not stop the production but will slow down the production rate. The phenomenon is reported here. To ease the melting of the silicon rod with many materials mixed, the surface was so designed to have a good absorption coefficient from the sunlight to cause a rapid melting as short as a few seconds, so that for a fresh rod, the initiation of the operation is rather easy. However, the solidified surface due to a short term clouding will not be so easy to be re-melted after the sunshine is resumed. The re-melting time would sometimes take up to one minute or longer. This is of course due to the less absorption coefficient for the solidified surface of the rod. In order to reduce such short term clouding, it is preferred to choose the location of solar furnace to have more continual cloudless days with dry weather instead of mild weather.

As a main purpose, induction furnace is used to compensate the drawback of solar furnace. It can be used to treat the left-over silicon rod in the solar process, and it can also independently treat the raw rod with a continual industrial process regardless of the weather condition. With a well thermally insolated crucible, the heat may be used more efficiently. The experiments show that the production rate can reach 8 kg/h for a 150 kW furnace.

8. Conclusion

Following our primary work,[1] we further discussed two devices, solar furnace and induction furnace to be used to remove boron inside silicon as strong radiation producers. The strong radiation is used for reaction catalysis to speed up the process to ensure the removal efficiency of boron and reduce the loss of silicon. According to the postulated Arrhenius–Ho high temperature photo-chemistry formula, sufficient temperature must be reached to meet the required photon flux and photon average energy for the catalysis effect. Since this temperature is much higher than the melting point of silicon, many of the measures have to be taken to ensure a good purification result, a high production rate and a reasonable yield. With all these efforts, we developed a low cost and highly efficient technique to remove boron from silicon for the production solar grade feedstock. This technique has at the moment been implemented in field. A number of industrial projects scattered in different places of the country, including the 4000 ton per year silicon project in Jinzhou, Liaoning Province of China have been well established.

Silicon is one of the richest elements on the Earth, the key issue to turn it into photovoltaic material is to purify the raw silicon and the major obstacle is to remove boron. An easy way to separate silicon and boron would be a breakthrough for a new route of releasing a great source of energy locked in this planet. The method of strong radiation catalysis may cast some light for this new alternative.

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