

# Development and Situation of Boron Removal from Solar Grade Silicon

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**Abstract**—In recent years, more and more attentions have been paid to the research of producing solar grade silicon by the metallurgical method, boron removal has always been difficult and important in various technologies. In this paper the recent research on removing boron is summarized. The boron removal is classified by the different forms of boron in removing boron: gaseous-boron removal, solid-boron removal and electrorefining-boron removal. The principle and outcomes of each boron removal craft are surveyed and compared, the possible application prospect is predicted.

**Keywords**- Metallurgical grade silicon; solar grade silicon; gaseous-boron removal ; solid-boron removal ; electrorefining-boron removal

## I. INTRODUCTION

For the past few years, with the developing of the photovoltaic technology and industry, it is more urgent to produce solar grade silicon. The Siemens' method is the main technique to make polycrystalline silicon, which has complex procedures, and consumes more. The metallurgical method as a new technology has been attracted the researchers' attention, for it is low cost. However, there are many impurities and defects, such as the impurities of transition metal, boron and phosphorus, the crystal boundary, dislocations, microdefects, etc., which is considered to be the key reason for low efficiency of photoelectric conversion. For the transition metal impurities, they are easy to be removed by repeated dephlegmation/segregation, owing to their low segregation coefficients. While boron and phosphorus, which segregation coefficients is near 1, are difficult to be

removed use the same method. Especially, boron, located in a diagonal position with silicon in the periodic table, has the similar characters to silicon. Hence, the impurities of boron is one of the bottleneck constraints in the progress of polysilicon batteries. For the moment, many methods to removing boron in silicon have been proposed, but there is still no large-scale production commercialization. In this paper, we introduce the methods and principles of boron removal from solar grade silicon, from the aspects of gaseous-boron removal, solid-boron removal, and electrorefining-boron removal. Then, we made an analysis and comparison of these methods, and look forward the application prospects of these methods.

## II. INFLUENCE OF BORON IMPURITY TO THE PERFORMANCE OF SOLAR CELL

Boron is the shallow level impurity in silicon, as a general dopant to control the electrical performance, and is the acceptor element in polycrystal silicon solar battery, which exists mainly the replace sites and interstitial sites of silicon atoms.<sup>[1]</sup> When an excess of boron stay in the materials, the metastable defects and deep level defects can form, which will capture the minority carriers as recombination centers, impact the lifetime of the minority carriers, and reduce the efficiency of the polycrystal silicon solar battery. It is widely believed that the defects of boron in silicon are the metastable defects of B<sub>2</sub>O and the deep level compounds of B<sub>2</sub>Fe, resulting from B, O, and B, Fe.<sup>[2]</sup> The working principle of solar battery is as following. When the sunlight irradiates on the p-n

junction, the semiconductor can absorb the energy higher than the energy gap and excite electrons to generate the non-equilibrium carriers, electrons and holes. These non-equilibrium minority carriers can be separated by the internal electric field, and assembled on the up and down poles of the solar cell to provide current to the external load. Part of the non-equilibrium carriers can recombine with the deep level of impurities and defects during the transfer process. Due to there are 3 electrons in the outermost layer of boron, it is easy to absorb an electron, which makes the strong recombination ability of boron to the minority carriers. Meanwhile, in the preparation of polycrystal silicon, the crystal defects caused by impurities is one of the main reason for the minority carriers' recombination. Therefore, excessive boron removal from solar grade silicon to get an appropriate concentration range, both can regulate the electronic features, and can control the minority carriers' recombination, which is a problem for the researchers. Besides, boron in silicon has stable physical prosperities, making the boron removal more difficult.

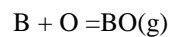
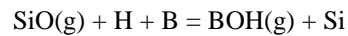
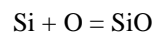
### III. METHODS AND PRINCIPLES OF BORON REMOVAL FROM SOLAR GRADE SILICON

The segregation coefficient of Boron is 0.8, near 1. Hence, it is hard to remove boron by directional solidification. According to the characters of boron, there are different methods. From the aspect of boron form, the common methods are gaseous-boron removal, solid-boron removal, and electrorefining-boron removal.

#### A. Principle and Main Technology of Gaseous-boron Removal

The boride during the boron removal is gaseous at the silicon melt temperature, which is named as Gaseous-boron removal. This method, using the traditional steelmaking process for reference, oxidizing gases are bubbled into silicon melt. The frequently-used gases are argon and oxygen, argon and water vapor, argon and ammonia, hydrogen and water vapor, argon and hydrogen, etc. That means one gas is used as carrier, the other oxide gas (water vapor, or the mixture of  $H_2$  and  $O_2$ ) or power

( $SiO_2$ ) are bubbled into silicon melt at a certain speed and pressure. Then, the oxide gas can react with the surface impurities (B, C) of silicon melt to produce volatile compounds with low boiling point (such as B<sub>2</sub>O, BO, CO). Therefore, the boron impurities are removed in the form of volatile gases. The reaction equations are in detailed:<sup>[3]</sup>



The reaction need to be processed in the vacuum system, in order to vent the volatile gases by the carrier gas or vacuum. The carrier gas can also promote the melt convection, accelerate the diffusion of impurities, increase the speed of chemical reaction, and is advantage to the impurity removal. For now, it is the hot spot in the metallurgical grade boron removal. However, it still has some problem, such as, the ratio and speed of the gases, and the way of air inlet. The diffusion effect and the reaction extent of gases in the silicon melt are also less than satisfactory, which has an influence on the boron removal. Moreover, the affinity of silicon and oxygen is close to that of the boron and oxygen, and the method can not only remove the boron, but also the silicon. Hence, it is hard to meet the need of the solar grade silicon only via the gaseous-boron removal.

Recently, the methods of gaseous-boron removal mainly contain heat exchange method, plasma oxidation purifying method, plasma water treatment to remove boron, and oxidation purifying technology, etc.

C.P. Khattak et al. have used the heat exchange method to reduce the concentration of boron impurity to 0.3 ppm.<sup>[4]</sup>

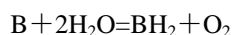
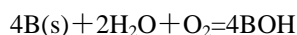
Their main technology is as following: in the modified heat exchange stove, in vacuum condition, the metallurgical grade silicon was heated to be silicon melt. Then, oxidizing slag forming constituents and wet hydrogen were insufflated into the silicon melt. Through the slag forming, gas reaction, purifying and directional solidification, the boron removal can be realized. The polycrystalline silicon produced by this method is the

most commercially-viable solar grade polycrystalline silicon, which is restricted to be mixed used with the product by the Slemens' method.

Plasma oxidation purifying method also belongs to the gaseous-boron removal method, which is used under the plasma condition. The oxidizing gases bubbled into silicon melt can decompose O and H to react with boron. Then volatile compounds containing B are removed. C. Alemany and his group combined the plasma arc smelting and electromagnetic stirring technique, used the ion beam to meltdown the silicon, inlet  $H_2$ 、 $O_2$  and  $H_2O$ . The boron in silicon can become BOH、BO、BH, which is easy to volatile. The mass concentration of B can be reduced from  $15 \times 10^{-6}$  to  $2 \times 10^{-6}$ .<sup>[5]</sup>

The company of Kawasaki Stell has developed the plasma water treatment to remove boron. They used electron beam melting, plasma arc melting and directional solidification. Electron beam melting can remove P by vacuum volatilization. Plasma water treatment can remove boron via oxidization. Twice directional solidification can remove the metal impurities. Then, the concentration of B, P can be reduced to  $1 \times 10^{-7}$ .<sup>[6]</sup> Many researchers have lucubrated on the plasma beam for boron removal. The studies show that the appropriate gas composition and content plays an important role in the boron removal. Above all, in this method, the high temperature make B violate much easier. However, the equipment in this method, is complex, and the cost is high.

In the plasma oxidation purifying method, the oxidizing gases  $O_2+H_2O$ , and  $O_2$ , and carrier gas Ar are mixed and inlet to the silicon melt. The oxide gas can react with B to form volatile compounds with low boiling point. The main reaction equations are:



At the high temperature ( $>1685K$ ), in the wet gas (Ar- $H_2O-O_2$ ), B,  $H_2O$  and  $O_2$  can react to produce the violated gases, BOH, and  $BH_2$ . The volatility of BOH is more than 10 times than that of other oxides of boron at the high temperature. Even at a low temperature, the volatility of

BOH is still strong. At the same time, boron can also react with  $O_2$  to form BO、 $B_2O_3$ 、 $B_2O$ 、 $BO_2$ 、and  $B_2O_2$ , which are volatile gases and can be removed. It should be noticed that the silicon can be oxidized to be  $SiO_2$  and  $SiO(g)$ , leading to the loss of silicon. Therefore, the key of the method is to control the condition of the oxidization, to only remove boron. The thermodynamics calculation shows that when the temperature is higher than 2200K, the affinity of boron and oxygen is much larger than that of the silicon and oxygen. Hence, to make sure boron removal from the metallurgical grade silicon, while reduce the loss of silicon, the process must be implemented in the low vacuum with oxidizing atmosphere and keep the temperature of the silicon melt at 2286-2320K.

#### *B. Principle and Main Technology of Solid-boron removal*

Solid-boron removal, mainly refers to the slag-boron removal. The slagging agent, which has an affinity for the impurities, are added into the silicon melt to react with the impurities. Then, the stable compound slag phase can be formed, which can sink into the bottom of the silicon melt or float on the surface of the silicon melt, due to it density is higher or lower than that of the silicon melt. After sieving and pickling, the boron compound slag will leach. In the current industrial silicon refining outside the furnace,  $SiO_2$  and  $Na_2O$  are used as the main ingredients of slagging agents. For the preparation of solar grade polycrystalline silicon, another method is as followed: a certain amount of  $BaCO_3$ ,  $BaO$ , or  $Ba(OH)_2$  were added into the silicon melt at 1500 ~2000°C for several hours. After cooling and crushing, the impurities (Al、P、B、Fe、Ti、Cr、V, and Ni) in silicon can be leached by dilute mineral acid. The content of B can be reduced from 26.1 ppm to less than 5 ppm. According to the relevant study, add alkaline slag agent or sulfide or other system into the silicon melt, can also remove boron. Besides, some researchers have studied the balance coefficient of B in silicon. The results show that during the silicon thermal oxidation process, because B has different balance coefficient with that of Si, B can be absorbed from Si to

SiO<sub>2</sub> layer, leading to reduce the impurities of Si in the interface of SiO<sub>2</sub>/Si. The difficulty of slag-boron removal is how to choose the slagging agent. The appropriate slagging agent, can not only reduce the content of impurities, but also avoid to bring new or other obstinate impurities. What's more, the reaction kinetics, the spread and the separation factor of the impurities, are the influence factors for slag-boron removal.

K.Suzuki et al. have analyzed the thermodynamic mechanism of B in the slag metal system, and found that the slag aid CaO-SiO<sub>2</sub>、CaO-MgO-SiO<sub>2</sub>、CaO-BaO-SiO<sub>2</sub>、and CaO-CaF<sub>2</sub>-SiO<sub>2</sub> can efficiently increase the distribution coefficient of B (the content of B in slag system/ the content of B in the silicon melt). The distribution coefficient of B will increase with the increase of alkalinity.<sup>[7]</sup> RYOUJINOGUCHI et al. have studied the activity coefficient of B in silicon, and the interaction coefficient of B and N. They predicted the activity of BO<sub>1.5</sub> in the melting system of CaO-CaF<sub>2</sub>-SiO<sub>2</sub> and CaO-MgO-SiO<sub>2</sub>, and the possibility of boron removal.<sup>[8]</sup>

Solid-boron removal mainly refers to slag refining. Nippon steel corporation can reduce the content of B in silicon below  $0.2 \times 10^{-6}$  by slag refining. Firstly, add the carbonate or bicarbonate oxidant including Na、Ca alkali metal or alkaline earth metal to the molten silicon, the boron impurities would be oxidized. Then, the slag aid (such as SiO<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, CaO, and Al<sub>2</sub>O<sub>3</sub>) was added into the molten silicon to make the boron oxide to be borosilicate slag phase. At last, the borosilicate slag could be removed. Cai et al. used the gas-slag refining method to reduce the content of B from  $10 \times 10^{-6}$  to  $0.23 \times 10^{-6}$ . At first, add the fore melt Na<sub>2</sub>O-CaO-SiO<sub>2</sub> slag aid, with the mass ratio of 15:55:30 orderly to the molten silicon. At the same time, the mix gas of Ar and H<sub>2</sub>O was inlet into the molten silicon. Then, one part of the B impurities was oxidized to become BOH by gas, while the other B impurities was oxidized to form B<sub>2</sub>O<sub>3</sub>. B<sub>2</sub>O<sub>3</sub> changed into the slag phase to be borosilicate, which could be removed. For the slag boron removal, it need large amount of slag

aid, and even repeat slag, which limit its application in mass production. Moreover, the slag aid can bring new impurities to silicon.

### C. Principle and Main Technology of Electrorefining-boron Removal

The principle of electrorefining-boron removal is based on the electronegativity difference of each element. In the process of electrolysis, the element with smaller electronegativity than that of silicon will strand at the anode, while the element with larger electronegativity than that of silicon will not separate out form the cathode to enter into the electrolyte. Hence, the impurities can be removed. In the periodic table, the electronegativity of B (2.04) is larger than that of Si (1.90), which insure the implementation of boron removal. But there are some electrolytic impurities in the obtained silicon. Due to the pollution of electrolyte and cell wall, it is hard to meet the requirement of solar grade silicon. The 4N silicon can be gotten only in the lab.

Jia's group have raised a new method "three layers of liquid molten salt electrorefining-polycrystalline silicon", according to the theories of the high purity aluminum production and electrorefining. They used the Cu-Si alloy as the anode and silicon source. Owing to the difference of deposition potential between the impurity and silicon, the Metallurgical grade silicon can be electrorefining via controlling the electrolytic process condition and parameters. The high purity silicon can be obtained from the fluoride molten salt by electrorefining at the temperature below the silicon melting point. The boron content is reduced from 12.7 to 2.2 ppmw, and the phosphorus content is reduced from 98.6 to 4.1 ppmw, which proves the electrorefining-boron removal method is effective and feasible.

## IV. CONCLUSION

With the development of the times, the need for solar grade silicon grow bigger. The technology for preparation of high purity silicon has attracted more and more attention. The removal of boron from silicon is one of the problem. Thermal plasma-boron removal, heat exchange,

slag oxidation refining,  $O_2+H_2O$  and  $O_2$  atmosphere oxidation refining, and electrolytic refining can remove boron to a certain extent. However, the above methods have not studied systematically the state of boron in silicon, and are lack of further study for the whole process. If the fundamental problems can be well researched, the boron removal technology can be promoted towards low cost and high efficiency.

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