Review of New Technology for Preparing Crystalline Silicon Solar Cell Materials by Metallurgical Method

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Abstract. The goals of greatly reducing the photovoltaic power cost and making it less than that of thermal power to realize photovoltaic power grid parity without state subsidies are focused on in this paper. The research status, key technologies and development of the new technology for preparing crystalline silicon solar cell materials by metallurgical method at home and abroad are reviewed. The important effects of impurities and defects in crystalline silicon on its properties are analysed. The importance of new technology on reducing production costs and improving its quality to increase the cell conversion efficiency are emphasized. The previous research results show that the raw materials of crystalline silicon are extremely abundant. The product of crystalline silicon can meet the quality requirements of solar cell materials: Si ≥ 6 N, P < 0.1 ppm, B < 0.08 ppm, Fe < 0.1 ppm, resistivity > 1 Ω·cm, minority carrier life > 25 μs; cell conversion efficiency of about 19.3%, the product costs <10 dollars / kg, the product energy consumption < 30 kwh / kg. The existing problems are pointed out. The prospect of the new metallurgical process with low cost, low energy consumption, low carbon and sustainable development are prospected.

1. Introduction

Solar photovoltaic power generation utilizes the photovoltaic effect of semiconductor materials to directly convert solar radiation energy into electrical energy. The core device that performs this conversion is a solar cell made from the semiconductor material. Crystalline silicon (including polysilicon and monocrystalline silicon) is the most ideal semiconductor material at present [1]. As the cost of the crystalline silicon solar cell materials solar cell materials, also known as photovoltaic materials that accounted for about 90% of market share of solar cell materials has occupied the largest proportion of the cost of photovoltaic power, so the development and application of new process for preparing highly efficient crystalline silicon solar cell materials at low cost has attracted increasing international attention [2].

Polysilicon accounted for more than 70% of the global market share of crystalline silicon. In recent years, Due to the introduction of the new technologies of continuous fast pulling monocrystalline silicon and diamond wire cutting silicon wafer, the cost of monocrystalline silicon wafer is approaching than that of polysilicon wafer. High quality monocrystalline silicon has much favoured by the market [3,4]. The breakthrough of a new technology of casting quasi-monocrystalline silicon is now
a compromise to solve the difficult problem of low cost but poor quality of polysilicon and good quality but high cost of monocrystalline silicon. Its quality stability of large-scale production and process production costs has been further optimized.\cite{5} The new technologies of polysilicon such as black silicon to produce PERC cells, silicon ribbon made from silica in the liquid transmission or made of polysilicon has been also introduced to reduce the cost of polysilicon materials.\cite{6,7}

Nowadays, the major methods of producing polycrystalline silicon in the world are chemical and metallurgical methods. Metallurgical methods is a series of technologies that silicon is purified by metallurgical refining technologies such as oxidation slagging, oxidizing volatilization, plasma smelting, vacuum evaporation, electron beam smelting, directional solidification, low temperature alloying solidification, acid leaching and so on. In the purification process of metallurgical methods, silicon element does not participate in chemical reactions, and separated from impurities element by the difference of physical and chemical properties of silicon and impurity elements. Metallurgical methods with low cost, low energy consumption, low carbon, low investment, safe, sustainable development and the incomparable competitive advantage over chemical methods have achieved unprecedented progress.

The innovation team led by academician Yongnian Dai of Kunming University of Science and Technology, etc. through a large numbers of long-term researches found that new metallurgical process for preparing high efficiency crystalline silicon solar cell materials at low cost is the most direct and effective way to greatly reduce the cost of photovoltaic power and make it less than or equal to the cost of traditional energy such as thermal power to realize the photovoltaic power grid parity without state subsidies. The study results show that crystalline silicon raw materials are extremely abundant, the product purity is Si ≥ 6 N, non-metallic impurities P < 0.08 ppm, B < 0.3 ppm, C < 4 ppm, O < 5 ppm, Fe, Al, Ca, Ti, etc. metal impurities < 0.1 ppm; resistivity > 1 Ω·cm, minority carrier life > 25 μs, which can meet the quality requirements of solar cell materials; the cell conversion efficiency of about 19.3%, the product energy consumption < 30 kwh / kg, the product costs <10 dollars / kg. The solar cells made of crystalline silicon materials by metallurgical method have been built a megawatt-class power station and gone well.\cite{8-29}

Since the development of metallurgical method, a variety of typical metallurgical processes have been formed, but it has not taken full advantage of its technical advantages for large-scale production, so further research is needed.

2 New Metallurgical Processes

2.1 The technical route
The technical route of new metallurgical technology is summarized in Figure 1, which includes the following four parts: metallic silicon preparation (Figure 1. part 1–2), polysilicon preparation (Figure 1. part 3–8), crystal growth (Figure 1. part 9–13) and wafer preparation (Figure 1. part 14).

The technical route of new metallurgical process depends on the type of impurities, content, occurrence and the differences of physical and chemical properties of impurities element and silicon element in metallic silicon. Non-metallic impurities B, P is difficult to remove. As the segregation coefficient of B is 0.8, close to 1, it cannot be removed by directional solidification method. B is the main substitute of silicon atoms in the silicon, and the acid leaching is not easy to remove. The vapour pressure of boron is close to that of silicon, and it is difficult to remove by the vacuum melting. However, there are great differences in properties of vapour pressure of B oxide and Si, and the properties of B in the segregation aspects is very different from that of Si, that is, the introduction of oxidizing substances into the molten silicon can make B to convert into a larger vapour pressure oxide or hydroxide gas to be removed. Or the distribution coefficient of B in the added oxidizing species system is much greater than that of B in Si, so as to achieve the effective separation of B and Si.\cite{9} Metal impurities, especially heavy metal impurities such as Fe can be effectively removed by directional solidification. In a word, Impurities and defects in crystalline silicon seriously can affect
the performance of crystalline silicon materials and cells [10], so the new metallurgical technology through the integration of technique reduce the cost of removing impurities and meet the quality requirements of solar cell materials [11].

**Figure. 1.** Schematic diagram of the technology route of new metallurgical process.

### 2.2 Key technologies and its development

The key technologies and development of new metallurgical process are listed in Table 1.

**Table 1.** Key technologies and development of new metallurgical processes.

| Key technologies and development of new metallurgical processes |
|---------------------------------------------------------------|
| 1 Metallic silicon preparation technologies and its development [11–13]. |
| 2 Polysilicon preparation technologies and its development |
| · Oxidative refining: Oxidative slagging, remove Ca, Al, P, B, etc. [8,14]. Oxidative volatilization (plasma), remove B [8]. |
| · Vacuum evaporation refining: Vacuum evaporation, remove P, Al, Ca, etc. [8,15]. Electron beam melting, remove P, Al, Ca, etc. [8,16]. |
| · Segregation refining: Directional solidification, remove Fe etc. [8,17]. Acid leaching, remove Fe, P etc. [8,18]. Low temperature alloying solidification; remove B and P [19]. |
| 3 Crystal silicon growth technologies and its development [9,20–21]. |
| 4 Crystalline silicon wafer preparing technology and its development [4,22]. |

#### 2.2.1 Metallic silicon preparation technologies and its development

Metallic silicon is usually made from carbonaceous reductant and silica (SiO₂) in the submerged arc furnace. The main reaction: \( \text{SiO}_2 \rightarrow \text{Si} + \text{CO} \). Silicon generated by the reaction
accounted for 66.67% of the total, and the rest is produced by dissociation (indirect, direct) of the remaining SiC. The melting temperature is about 1730 °C \[12\]. The volatilization loss of SiO and the residual amount of SiC should be reduced. The way to improve the quality of metallic silicon is selection of raw materials (silica and carbon reducing agent). The quality of silica: SiO\(_2\) ≥ 98%~99%, Fe\(_2\)O\(_3\) ≤ 0.15%~0.5%, Al\(_2\)O\(_3\) ≤ 0.2%~0.5%, CaO ≤ 0.~0.5%, P\(_2\)O\(_5\) ≤ 0.03%, total impurity ≤ 0.6%. In addition, the process of preparing high purity silicon by hydrogen as reducing agent for the thermal reduction of silicon dioxide is a development direction for low-cost, low-carbon technology route \[13\].

2.2.2 Polysilicon preparation technologies and its development

Oxidative refining. Cai et al. used a ternary system of 55% CaO-30% SiO\(_2\)-15% Na\(_2\)O, according to a certain proportion of slag and silicon, to introduce a gas of 99.5% Ar-0.5% H\(_2\)O at a flow rate of 18 L / min to the silicon melt for 90 min, the impurity boron content from 10 ppm down to 0.23 ppm to meet with the solar cell materials quality requirements, but did not make Al, Ca, P less than 0.1 ppm \[14\].

Vacuum evaporation refining. Zheng Song-sheng et al used vacuum induction melting 2h in the vacuum of 0.1~0.035 Pa and temperature 1773 ~ 1873 K to make the content of impurity P in silicon from 15 x 10\(^{-6}\) reduced to 0.08 × 10\(^{-6}\) meet the requirements of solar cell materials (P <0.1 ppm) \[15\].

Pires refined metallic silicon using acid leaching and not being any pre-treatment and found that the purity of silicon can be improved from 99.92% to 99.9998% by controlling the vacuum degree of electron beam melting in the range of 1 × 10\(^{-4}\) ~ 1 × 10\(^{-2}\) Pa \[16\].

Segregation refining. Directional solidification refining can remove the metal impurities such as Fe, Ni, V, Cr etc. in silicon to meet the requirements of solar materials is \[17\]. Dai Yongnian etc. applied acid leaching to treatment to exclude Fe to make it not recycled in the purification process of silicon \[8\]. Tomohito etc. found that Ca and P also had strong affinity, so the activity coefficient of phosphorus decreases in the silicon melt, resulting in the decrease of the solid partition coefficient of phosphorus, that is, the addition of Ca is helpful to reduce P in Si, And Ca\(_3\)P\(_2\) was deposited near the second phase CaSi\(_2\), Ca\(_3\)P\(_2\) could be removed by acid leaching \[18\]. Yoshikawa et al. calculated the partition coefficient of phosphorus in extremely dilute solution at the temperature from 1173 K to 1373 K. The calculated results show that the phosphorus and aluminium have strong affinity in the solid state, and in the liquid Si-Al alloy, phosphorus exists in the form of AlP, which can be effectively removed by directional solidification. K. Morita made use of silicon and aluminium waste to prepare solar grade silicon materials by low temperature solidification and the content of impurities in crystal silicon solar cells materials (ppm) were Fe 0.003, Al 0.00004, P 1 and B 0.1 \[19\].

2.2.3 Crystal silicon growth technology and its development

Due to the high cost of FZ (Floating zone, less used in photovoltaic industry. But now, China Zhonghuan Technology Co., Ltd. has been using fusion of FZ and CZ technology (FCZ method) to produce monocrystalline silicon for PV industry, and the cost of PV electricity of integrated new photovoltaic system is as low as about RMB 0.4 / KWH \[20\]. The growth of polysilicon eliminated the expensive fabrication process of monocrystalline silicon and easily made square ingot, to improve the utilization ratio of the material and the packing density of the battery template. Ribbon silicon pyoduced by the United States 1366 company has the conversion efficiency of commercial cells made of ribbon silicon is 19.3% and its preparation cost is only 40% of polysilicon wafers \[7\]. Silicon ribbon preparation process can realize the whole melting state of silicon to polycrystalline silicon solar cell material. The technology of casting quasi monocrystalline silicon combined with the advantages of CZ-Si and casting polysilicon can reduce the cost of PV power. The LID rate of cell produced by quasi monocrystalline ingot fell below 0.5% and its performance is more stable. The average conversion efficiency of solar cells was 17.6%. Silicon material utilization rate of about is 70%~90%. Quasi monocrystalline ingot cost is about RMB 60 yuan / kg which can make the whole production chain to reduce the cost of about 10%. The representative enterprise such as the GCL is focused on single crystal casting to type P into N type. Mass production of monocrystalline silicon ingot combined with diamond wire slicing technique can cut more thin silicon wafers. The black silicon
technology can solve the problem of surface texturing. N quasi-single crystal is the focus of future development [21].

2.2.4 Crystalline silicon wafer preparing technology and its development

The latest diamond wire slicing technology because of its environmental protection, high efficiency, thin film, thin wire technology makes the cost of monocrystalline silicon chip dropped sharply and rising market share. The proportion of crystal silicon diamond wire slicing will increase and become the mainstream of slicing technology. Advanced battery manufacturers such as Panasonic, Sunpower, Silevo, etc. have begun mass production of N-type 150μm battery. Japan, Swiss companies with diamond wire cutting single crystal or even 80μm, domestic Longji Limited by Share Ltd in 2014 took the lead in the application of diamond cutting line 110umN type single crystal wafers. The conversion efficiency of the N type HIT battery has been more than 22%. At present, the world class HIT cell laboratory conversion efficiency can reach 25.6%. The latest diamond wire slicing technology, such as cutting speed, thin wire diameter and thin film will be able to significantly reduce the cost of silicon wafer [4,22].

2.3 The typical metallurgical process

2.3.1 Japan JFE metallurgical process

The process is shown in Figure 2. Japan’s JFE Corporation under the support of the new energy and Industrial Technology Development Organization (NEDO) developed it in 1996. It consisted of a two-stage purification of MG-Si to SOG-Si: In vacuum, MG-Si is melted and P removed by electron beam, and then Fe and so on removed by directional solidification. In a vacuum-free Ar atmosphere, the plasma gun was used to heat, and oxygen and water vapour were added to remove B and C, and then the second directional solidification was carried out. Electron beam evaporation and plasma oxidation can reduce the concentration of B and P to 0.1 ppm, which solves the technical difficulties of purifying MG-Si to SOG-Si. The second directional solidification made metal impurities down to 0.1 ppm, the conversion efficiency of cells reached 14.1% [23].

![Figure 2. Japanese JFE metallurgical process of [23].](image)

2.3.2 Chinese ProPower’s metallurgical process

The process is shown in Figure 3. The solid-liquid ion exchanger is specially used for processing silicon material with more impurities in every production process. Vacuum melting equipment has the functions of vacuum melting, high temperature gas reaction and directional condensing. The furnace refining is first adding slagging agent in the induction heating furnace, blowing oxygen refining, slagging-off, molten silicon was poured into the insulation bag for directional solidification in order to obtain a purity of 4N
silicon metal (impurity total 100 ppm, wherein the total content of Fe, Al and Ca is about 80 ppm, P is about 5 to 10 ppm and B is about 1 to 2 ppm). The purity of 5N silicon was obtained by vacuum melting. The slagging agent and the oxygen blowing are continuously added under vacuum to oxidize impurities which are difficult to separate from silicon into compound slag floating on the surface of the silicon, part of the sink in the bottom of the crucible, part of the gas that drew out of the furnace by vacuum system. 6N monocrystalline silicon solar cell material was prepared by directional solidification and single crystal drawn, and the conversion efficiency was 17%. The total of investment is 1/6 only conventional Siemens, power consumption is 1/5 and cost is 1/3 [24].

2.3.3 Chinese Yongnian metallurgical process

The typical metallurgical process is shown in Figure 4. It is currently being verified in the implementation. The process removes boron by wet hydrogen blowing and removes phosphorus by vacuum evaporation. The molten silicon produced by the ore furnace first is refined to meet the requirements of the quality of metallic silicon to be directly poured into the double heating furnace at temperature 1450 to 1550° C, and respectively under normal pressure blows gas mixture (Ar, H2, H2O) oxidation refining and in vacuum (10⁻¹ ~ 10⁻³ Pa) evaporation refining until the B < 0.3 ppm, P < 0.1 ppm. The silicon melt flows into the holding furnace for directional solidification refining to removal of iron and other metal impurities. Finally, casting quasi monocrystalline silicon and cutting wafers that will be used for the preparation of high efficiency solar cells. The process characteristics: It is beneficial to the control of product quality and cost, especially for silicon metal factory to implement technical innovation and industrial upgrading. Double cycle heating furnace has a cycle of purification and on-line detection function. Casting quasi monocrystalline silicon ingot and diamond wire cutting silicon slicing can significantly reduce the production preparation wafers cost and improve the quality of products to ensure large-scale product quality to be stable and meet the quality requirements of solar cell materials. The process is energy saving and environmental protection [25].

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**Figure 3.** Chinese ProPower’s metallurgical process [24].
2.3.4 Other typical metallurgical processes

Other typical metallurgical processes are shown in Figure 5.

- **Norway Elkem metallurgical process** [26]

  MG-Si → Acid leaching → CaCO₃ slagging → Directional solidification → SOG-Si

  The concentration of B in MG-Si is 300 ppm and that of P is 100 ppm. The concentration of metal impurity is 150 ppm, the resistivity is 0.4–10Ω.cm. The process flow is simple, the production cost is low, the energy consumption is only 20%–25% of the Siemens method. The production silicon is mixed with the electronic-grade silicon by 25%–100%. The solar cell conversion efficiency is 15%–16.5%.

- **US Dow Corning metallurgical process** [27]

  In a vacuum environment of an improved heat exchange furnace. MG-Si was heated to a molten state, and introduced slagging agent, wet argon, water vapor and other gases into silicon melt and happened oxidation reaction and then directional solidification was carried out. By extending the refining time, the impurity concentration of B can be reduced to 0.34 ppm, but that of P can only be reduced to 7 ppm, and other impurity concentrations are lower than 0.1 ppm. The cost of polycrystalline silicon produced by the method is 2/3 of the improved Siemens method. The products with commercial value of PV1101 silicon, according to the proportion of 1:10, namely 1 copy of PV1101 silicon and 10 copies of polysilicon produced by chemical method mixed to use.

- **Germany Wacker metallurgical process**

  The acid leaching is adopted so that the metal impurities in metallic silicon went into the solution and then smelted the residue leaching and finally directionally solidified, the impurity removal effect is not published.

- **China’s vacuum metallurgical process** [28]

  The national engineering laboratory of vacuum metallurgy, Kunming university of science and technology proposed the process based on the distribution characteristic of impurities in metallic silicon based on directly from the metallurgical grade silicon preparing solar-grade silicon. The process is carrying out industrial test research. The process has been granted the national patent. The purity of product is close to 6N.

- **China’s Ningxia Silver Star metallurgical process** [29]

  The concentration of metal impurity Fe belongs to the deep level impurity, which will form a complex centre in the forbidden band of the crystal silicon and seriously affects the performance of the crystal silicon materials and solar cells. B and P belong to the shallow level impurity. Except doping, if the P content is high, the impurity compensation effect will be formed; if the B content is high, the B-O complex
will be formed with O and the Fe-B complex will be formed with Fe, which can reduce the minority carrier lifetime, lead to the light induced degradation of the cell and reduce the photoelectric conversion efficiency of the cell, so impurity B, P, Fe in matrix material of solar cell should be less than 0.3 ppm, 0.1 ppm and 0.1 ppm, respectively [14,15]. Other impurities such as non-metallic impurities O, C and metal impurities Ni, Cu, Au, Ag, etc. also have a significant impact.

Dislocations and grain boundaries exist mainly in polysilicon. Defects in Single crystal silicon are only dislocations. The effect of defects is introducing deep-energy levels in the forbidden band to form recombination centres, which not only affect the minority carrier life, but also affect mobility ratio and so on. Since most of the dislocations have a complex activity, at high temperature above 1100° C, the dislocation density in polysilicon can will be reduced. When the annealing temperature reached 1366° C, the dislocation density decreases rapidly and disappears completely [30,31].

In conclusion, the impurity and defect of monocrystalline silicon is lower than that of polycrystalline silicon, so its performance is better than that of polycrystalline silicon. The problem that the industry is difficult to overcome is light induced degradation (LID) of monocrystalline silicon cell. In recent years, LID of the newly developed and industrialized passivated emitter and partial rear contact (PERC) cells is up to 3% ~ 5%. The study indicated that boron oxygen (B-O) complex, C content in crystal silicon, segregation coefficient of oxygen in silicon, Fe-B on the decomposition and composite is the main influencing factors that results monocrystalline silicon cell degradation is serious than that of polycrystalline silicon cell degradation. The difference of CZ-Si and MC-Si attenuation with the same resistivity is caused by the change of O and C concentration. MC-Si grain boundaries and defects are more than CZ-Si, but the defects have little effect on LID [32-34].

2.5 The role of metallurgical method in solar photovoltaic power generation

Wang Shujuan concluded that the main variable quantities that affect greatly on the cost of photovoltaic power are initial investment and the annual generating capacity [35]. Due to the cost of PV components accounted for about 50% of the initial investment, so it is critical to reduce greatly the costs of preparing crystal silicon solar cell materials that account for relatively large proportion in the cost of components. If initial investment decreased by 10%, 20%, and 30%, respectively, the cost of photovoltaic power decreased by 8%, 17%, 25%. At the time, the photoelectric conversion efficiency of cell is increased by 1%, and the cost of photovoltaic power is decreased by 1%. If the generating PV-power capacity reduced by 10%, 20%, 30%, the cost of photovoltaic power will increase accordingly by 11.2%, 25.4%, and 49.9% [36]. Yang Dazhou found that the cost of polysilicon in crystalline silicon cell components and power generation systems decreased from 43% and 32% in 2008 down to 16% and 8% in 2014. Obviously, significantly reduce the cost and price of polysilicon raw materials will lead to a substantial decline in the cost of photovoltaic power [36].

The benchmark price of desulfurization of thermal power is now between RMB 0.25~0.5 /kWh, so there is still a certain distance between China's benchmark price of photovoltaic power and that of thermal power. The key technology innovation has a large space to reduce costs, and can get lower cost and higher efficiency of crystalline silicon material. During the periods of "13th Five-Year" in China, the new PV installed capacity of 150 GW. In terms of per watt needs crystalline silicon material 5g and the market share of crystalline silicon material by 80%, China market needs at least 600 thousand tons of crystal silicon material, and if its costs are controlled in RMB 50 yuan / kg, the photovoltaic grid parity can be achieved [37].

The energy consumption and CO₂ emissions of generating a kilowatt-hour of solar photovoltaic power were 1810.8 KJ and 0.0984 KG, respectively, compared to coal-fired power generation can reduce about 90.3% emissions of CO₂ [38]. Energy saving and emission reduction effect is remarkable.

2.6 Existing problems in new metallurgical process
The core problem of the new metallurgical technology is that the cost removal of boron and phosphorus in silicon is not low enough and the quality of low-cost product is not stable enough, so as has not yet played its technical advantages in large-scale production, such as expensive equipment, high-energy consumption and low productivity in the processes of removing impurity phosphorus by the electron beam and removing impurity boron by plasma. Removal of boron by oxidative slagging combined with oxidation volatilization, and removal of phosphorus by volatilization of vacuum induction melting are based on the principle of easy oxidizing of boron and easily volatilization of phosphorus, but when the concentration of boron and phosphorus is too low to the driving force of the removal process is very slow, it is difficult to achieve the effect of removing impurities. Low temperature alloying directional solidification technology can make B $< 0.3$ ppm, but failed to make P $< 0.1$ ppm. The Quasi-single crystal ingot technology can reduce the crystal defects, but the quality is not stable. SOG-Si of large-scale production by metallurgical method in foreign countries has been mainly used for blending materials. Only a small number of domestic products have been used for PV power generation. It is the key to the further development of the new metallurgical technology to seek low-cost boron and phosphorus removal technology [39,40]. The upstream and downstream enterprises of photovoltaic industry chain need close cooperation and continuous innovation.

3 Conclusions

Preparing high efficiency crystalline silicon solar cell materials at low cost by metallurgical method is the most direct and effective way to greatly reduce the cost of PV power. Now, the product purity is Si $\geq 6N$, the production cost $< 10$ dollars / kg, the energy consumption $< 30$ kwh / kg, and the solar cells made of crystalline silicon materials by metallurgical method have been built a megawatt-class power station and gone well. In view of the need of high-quality power plant, our first task is to play a technological advantage of new metallurgical process in large-scale production for producing high-quality crystalline silicon solar cell materials with the excellent performance of high purity, low resistance, long the minority carrier lifetime to make solar cells with high conversion efficiency, which can increasing annual power generating capacity and prolong the life of the PV system so as to finally reduce the cost of photovoltaic power and achieve the grid parity of photovoltaic power generation without state subsidies.

The key technologies of new metallurgical process have a large space to reduce the production cost. So the breakthrough of crystal silicon purification technology, Cz single crystal silicon preparation technology, casting monocrystalline silicon growth technology, low dislocation density and high efficient Polysilicon growth technology, thin slices of silicon cutting technology, the diamond wire cutting technology for casting polycrystalline silicon and other aspects need us to work harder and keep innovating.

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