# Optimization of the acid leaching process by using an ultrasonic field for metallurgical grade silicon*

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**Abstract:** In the experiment, acid leaching under an ultrasonic field (20 kHz, 80 W) was used to remove Al, Fe, and Ti impurities in metallurgical grade silicon (MG-Si). The effects of the acid leaching process parameters, including the particle size of silicon, the acid type (HCl, $HNO_3$, HF,) and the leaching time on the purification of MG-Si were investigated. The results show that HCl leaching, an initial size of 0.1 mm for the silicon particles, and 8 h of leaching time are the optimum parameters to purify MG-Si. The acid leaching process under an ultrasonic field is more effective than the acid leaching under magnetic stirring, the mechanism of which is preliminarily discussed.

**Key words:** purification; optimization; acid leaching; ultrasonic field; metallurgical grade silicon
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## 1. Introduction

The development of a low-cost process for the production of solar grade silicon (SoG-Si) of 99.9999% purity has been a hot topic of recent studies[1, 2]. The metallurgical method (vacuum induction melting[3], vacuum electron-beam refining[4], directional solidification technology[5], floating zone technique[6], etc.) will be the future of SoG-Si production because of its lower input, pollution, and energy consumption[7, 8]. Although effective in most cases, some elements such as Al, Fe, and Ti can still hardly be removed by a single directional solidification. Duo to its low work temperature, the acid leaching process needs less energy. However, the P and B that lead to a deterioration of the solar cell performance cannot be removed effectively by the acid leaching process[9]. Therefore, as a preliminary step before the metallurgical method, the acid leaching process is a suitable method for removing these elements.

The acid leaching process was first presented by Tucker in 1927[10]. In a patented process of 1961, Voos[11] proposed to obtain silicon suitable for microwave diodes by the treatment of pulverized MG-Si with $H_2SO_4$, aqua regia, HF, and other acids. Hunt introduced the removal of more than 90% of the impurities in MG-Si by leaching with aqua regia for 12 h at 75 °C in 1976[12]. Chu reported in 1983[13] that the best results were obtained by refluxing pulverized MG-Si of undefined grain size with aqua regia. The systematic basic research of acid leaching was conducted by Sakata in 2002[14] and Yu in 2007[15].

The ultrasonic treatment in liquids gives rise to cavitation and acoustic streaming effects. In recent years, many researchers have investigated the chemical effects of the ultrasonic field. Henglein introduced the historical development and modern aspects of sonochemistry in 1987[16]. In 1994, Mason[17] summarized the current trends in sonochemistry and showed that the acoustic cavitation was accompanied with other mechanical and physical effects. Gasgnier demonstrated the ultrasonic effect on various oxides and ceramics in 1995[18]. In 2006, Azevedo[19] showed that the generation of a variety of radicals and highly reactive intermediates lead by the presence of solvent vapor. Volatile solutes and other gas molecules within the bubbles may initiate other secondary chemical reactions in the liquid. In 2007, Ashokkumar[20] analyzed the effect of bubbles in an acoustic field and considered the sonochemistry simplified or accelerated reactions under normal conditions. In 2008, we[21] compared the acid leaching under an ultrasonic field with magnetic stirring and found that the ultrasonic field is helpful to increase the removal rate of metallic impurities in MG-Si.

In this paper, we systematically studied the effect of the particle size of the silicon, the acid type (HCl, $HNO_3$ and HF), and the leaching time on the purification of impurities in MG-Si, and verified the optimal parameters of acid leaching under an ultrasonic field. A possible reaction mechanism between impurities and acids under an ultrasonic field is proposed.

## 2. Experiments

### 2.1. Experimental materials

99.8% purity MG-Si was used in this experiment. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was adopted to measure the impurities in MG-Si. The measurement results show that Fe, Al, Ca, Ti, Cu, and Zn are the predominant metallic impurities in MG-Si, and their content is shown in Table 1.

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Table 1. Impurity content in MG-Si.

| Element | Fe | Al | Ti | Ca | Cu | Zn |
|---|---|---|---|---|---|---|
| Content (wt. %) | 0.23399 | 0.27098 | 0.0198 | 0.05752 | 0.00271 | 0.00006 |

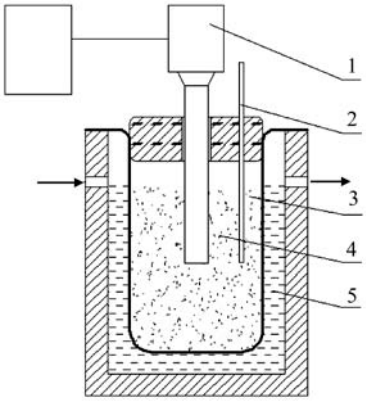


Fig. 1. Schematic of the experiment apparatus for acid leaching under an ultrasonic field: 1. Ultrasonic generator; 2. Thermocouple; 3. Acid solution; 4. Silicon particles; 5. Water-bath system.

To prevent silicon particles from passivating in the higher concentration acid solution, the concentration of HCl, $HNO_3$, and HF was diluted to 2, 2, and 4 mol/L, respectively.

### 2.2. Experimental apparatus

The experimental apparatus, schematically shown in Fig. 1, consists of an ultrasonic generator, a temperature control system, and a water-bath system. The acid solution and the silicon particles are placed in the leaching tank.

An intermittent ultrasonic field is utilized with an interval time of 5 min, where the power is 80 W and the frequency is 20 kHz. To increase the reaction rate and to reduce the volatilization of the acid solution, a water-bath system is used to keep the reaction temperature at 50 °C. For comparison, magnetic stirring is used after the silicon particles were placed into the acid solution with a stirring speed of 180 rpm.

### 2.3. Experimental procedure

At first, the MG-Si was pulverized to particles. The ferromagnetic impurities accompanying the pulverization process should be removed from the silicon particles by a magnetic separation technology. Then, the silicon particles were immersed in acetone to remove the oil film before the acid leaching process. After that, the silicon particles were leached by different kinds of acids for 8, 12, 16, 20, and 24 h at 50 °C under an ultrasonic field and with magnetic stirring, respectively. It should be noted that the silicon particles and the acid solution should be stirred homogeneously before the intermittent ultrasonic field is applied. After the acid leaching, the silicon particles were filtered and washed with deionized water.

The distribution of the impurities was analyzed by electron probe microanalysis (EPMA-1600) and the content of the impurities in the silicon particles was measured by ICP-AES (Optima 2000DV). The morphology of the silicon particles was characterized by a scanning electron microscope (SEM, JSM-5600LV).

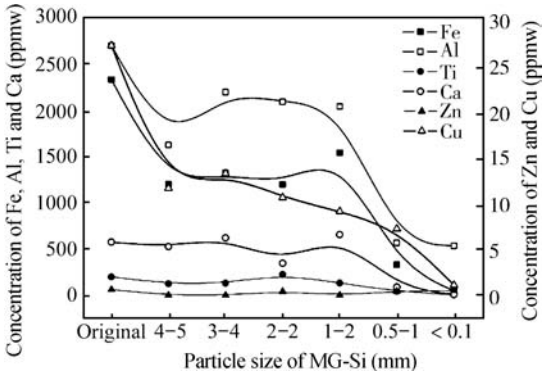


Fig. 2. Concentration of dominant impurities after HCl leaching under an ultrasonic field for 8 h.

## 3. Results and discussion

### 3.1. Particle size

To find the suitable particle size of MG-Si in the acid leaching process, the MG-Si was pulverized to 4–5, 3–4, 2–3, 1–2, 0.5–1, 0.1–0.5 mm, and less than 0.1 mm, respectively.

On the one hand, the concentrations of the impurities in the silicon particles were measured after HCl leaching for 8 h, as shown in Fig. 2. When MG-Si was pulverized to 1–5 mm, the impurity concentrations reduced to some extent. When the silicon particles were pulverized to less than 1 mm, all impurity concentrations reduced dramatically after a HCl leaching of 8 h. When MG-Si was pulverized to particles having sizes of 0.5–1 mm, the removal rates of metallic impurities increased by more than 70%. Furthermore, when pulverized to less than 0.5 mm, the removal rates increased by more than 90%. In this period, the smaller the particle size is, the higher the removal rate of the impurities will be. When the particles size was less than 0.1 mm, the removal rate did not decrease any more.

On the other hand, the distribution of impurities was measured by EPMA, as shown in Fig. 3. The metallic impurities Fe, Al, Ca, Ti, Cu, and Zn concentrate at the grain boundaries, while the other impurities, such as C, O, and P, are uniformly distributed over the grains. This is due to the fact that the metallic impurities have a lower solubility in the solid than in the molt because the Gibbs energy change of mixing for the solid state rapidly increases with a minute amount of impurities added after exceeding the minimum value[22, 23]. And it can be deduced from Fig. 3 that the grain size of MG-Si is about 1 mm. Because of the segregation of these metallic impurities, the concentration in the grain boundary is lower than that in the grain. Consequently, these impurities are exposed

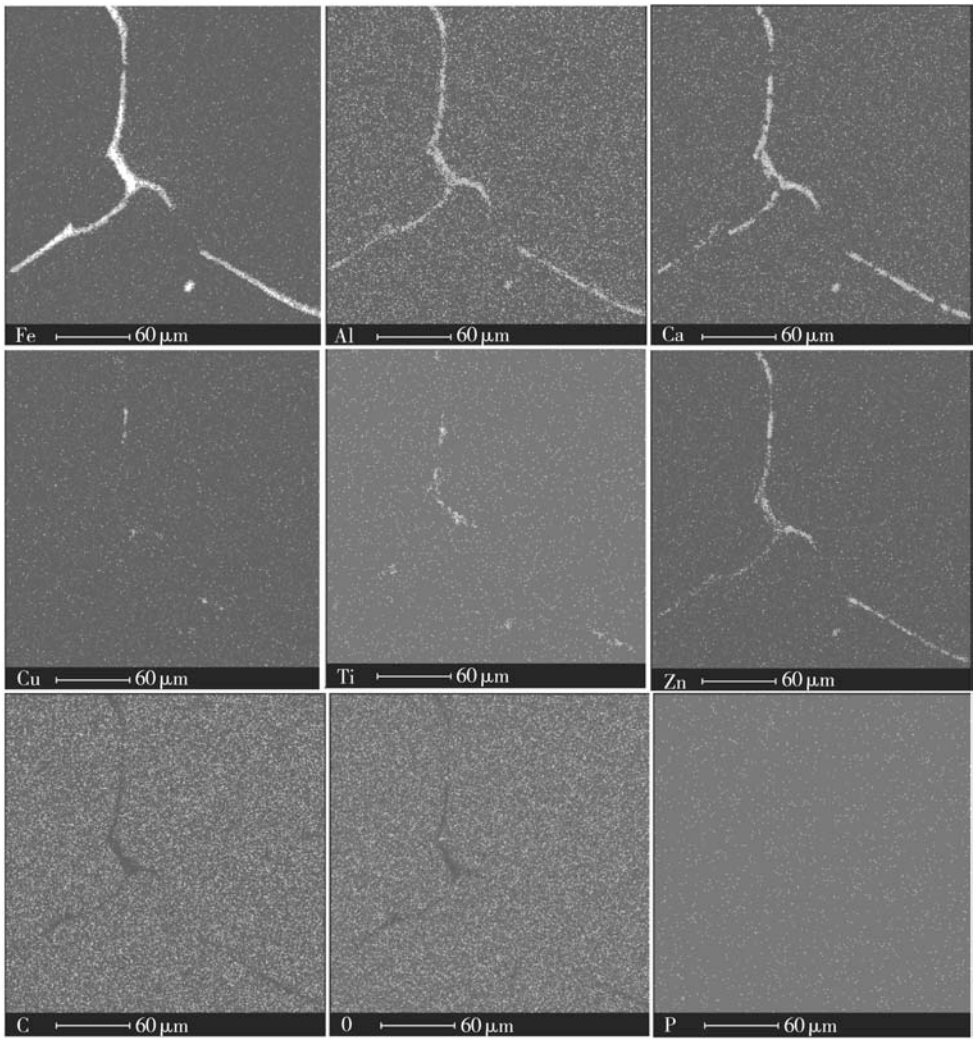


Fig. 3. EPMA photographs of the distribution of dominant impurities in MG-Si.

on the surface of the grain when silicon ingots are broken into grains. Silicon particles with a size of less than 1 mm are suitable for acid leaching.

Based on the analysis mentioned above, it can be deduced that the appropriate size for particles in the acid leaching process is about 0.1 mm.

### 3.2. Acid type

In order to confirm the purifying effect of different acid leaching processes, silicon particles of about 0.1 mm were leached by HCl, $HNO_3$, and HF under an ultrasonic field, respectively. Figure 4 shows the concentrations of the impurities Fe, Al, and Ti after acid leaching for 8 h under an ultrasonic field.

It can be seen that the removal efficiency of Al and Fe is the highest when leaching with HF, followed by HCl. Using $HNO_3$ leads to the worst performance. The removal efficiency of Ti is the highest when leaching with HCl, followed by HF. In this case, $HNO_3$ again leads to the worst performance. Therefore, the effect of HF and HCl leaching under an ultrasonic field on the purification is better than that of $HNO_3$ leaching. As a preliminary step of the metallurgical method,

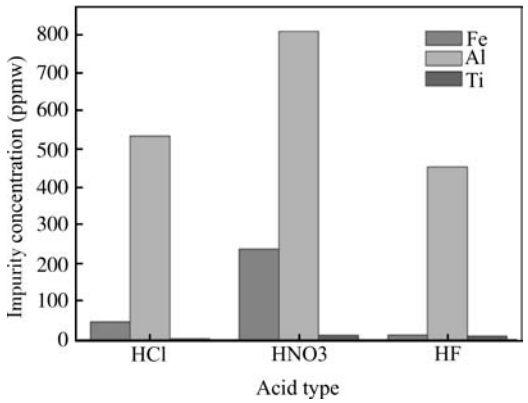


Fig. 4. Concentration of impurities after leaching by HCl, $HNO_3$, and HF.

HF or HCl leaching under an ultrasonic field is an effective method to remove the Fe, Al, and Ti impurities. Considering that silicon has a high corrosion resistance to most acids except for HF, HCl is selected to leach the silicon particles in the following experiments in order to reduce the waste of silicon.

### 3.3. Leaching time

In order to remove the impurities from MG-Si, the silicon particles were immersed in HCl for a certain amount of time.

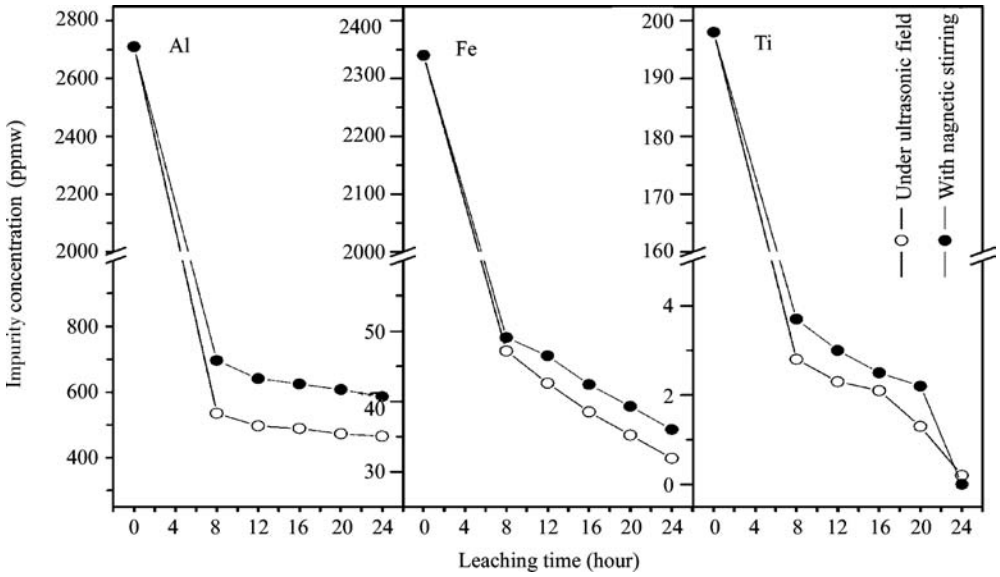


Fig. 5. Relation between concentrations of Fe, Al, and Ti and the leaching time.

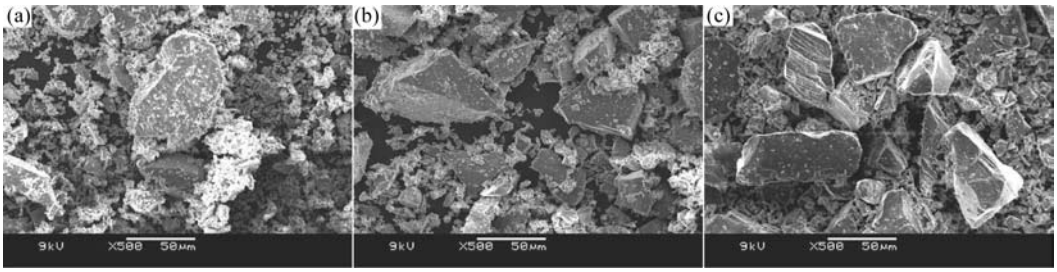


Fig. 6. SEM morphology of silicon particles: (a) 0 h; (b) 8 h; (c) 24 h.

Figure 5 shows the relations between the concentration of the impurities and the leaching time.

When an ultrasonic field is used in the HCl leaching process, the concentration of metallic impurities adhering to the silicon particles obviously reduced after 8 h of HCl leaching. Especially the concentration of Fe decreased from 2339.9 to 47.2 ppmw, and the concentration of Ti decreased from 198 to 2.8 ppmw. When the leaching time is prolonged, the content of metallic impurities does not reduce greatly. The HCl leaching process with magnetic stirring showed the similar tendency. Compared to the above two kinds of HCl leaching processes, the concentration of impurities after HCl leaching with an ultrasonic field is lower than the concentration after magnetic stirring.

From the analysis mentioned above, it can be found that the the concentration of the impurities decreases with the acid leaching time. Considering the production efficiency and the removal efficiency of impurities, the optimum leaching time is determined to be 8 h.

### 3.4. Morphology of silicon particles

Figure 6 gives the SEM morphology of silicon particles after HCl leaching for 0, 8, and 24 h under an ultrasonic field, respectively.

From this figure, the surfaces of the silicon particles are covered with impurities before the particles were leached with the acid. When silicon particles were HCl leached for 8 h, the concentration of the impurities was reduced to a great extent, but there were a certain amount of reaction produces covering the surface of particles. The reaction products are removed when the leaching time was increased from 8 to 24 h. In conclusion: the morphology of silicon particles after HCl leaching in an ultrasonic field is cleaner than that of the raw materials.

## 4. Discussion

During the HCl leaching process, the impurities exposed on the surface of the silicon particles would dissolve into the acid. Owing to defects and slits under the surface of the silicon particles, they have no chance to directly react with the HCl due to the interfacial tension and the wettability of the silicon particles. When an ultrasonic field is used in the acid leaching process, the mechanical interaction between the sound waves and the liquids would lead to the phenomenon of cavitation and acoustic streaming. The mechanism of HCl leaching under an ultrasonic field is schematically shown in Fig. 7.

Because many gas molecules gather in defects and cracks of the MG-Si, they can easily turn into the nuclei for ultrasonic cavitation[24]. The cavitation bubbles near the defects and cracks will first grow by directional diffusion. As they reach the resonance size range, they collapse, resulting in the generation of a high temperature near the bubbles[20]. The acoustic cavitation is also accompanied by other mechanical and physical effects, such as the formation of shock waves and turbulent motion of the liquid. Due to these ultrasonic field

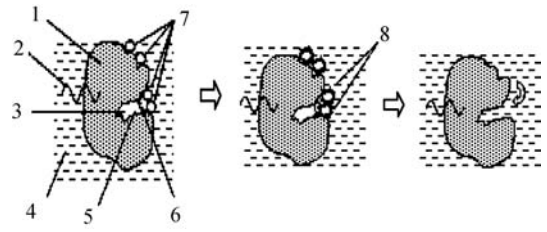


Fig. 7. Reaction mechanism of acid leaching under an ultrasonic field: 1. Silicon particle; 2. Ultrasonic field; 3. Grain boundary slit; 4. Acid solution; 5. Metallic impurities; 6. Surface tension; 7. Cavitation bubbles; 8. Collapse.

effects, the wettability of the impurities was enhanced, and the interfacial tensions were broken during the acid leaching process, allowing the impurities, which are exposed in the defects and slits, to react with the acid solution.

The reaction between metallic impurities and an acid is an exothermic reaction, which can be expressed by Eq. (1). When an ultrasonic field is used in the acid leaching process, the high temperature and the high pressure generated by the ultrasonic cavitation will theoretically accelerate the reversed reaction. However, in this experiment, the opposite results is seen. It is because the solution is induced a high temperature and a high pressure in microscopic scales, the solution is showed at normal temperature and pressure in macroscopic scales. The high temperature and the high pressure in the microscopic scales accelerates the reaction rate. The normal temperature and the pressure in the macroscopic scales ensures a positive reaction.

$$2\mathrm{M} + 2x\mathrm{HCl} \longrightarrow 2\mathrm{MCl}_x + x\mathrm{H}_{2(\mathrm{g})} + \mathrm{Q}. \quad (1)$$

Therefore, in the HCl leaching process, the impurities present a solid and the acid present a solvent. The reaction between the impurities and the acid is improved when an ultrasonic field is generated in the acid solution. As a result, the reaction between the metallic impurities and the HCl acid under an ultrasonic field is more complete.

On the other hand, the metallic impurities adhering to the surface of the silicon particles are consumed by the acid for a prolonged leaching time. The reaction rate is mainly determined by the diffusivity of the internal impurities in the silicon particles. When the silicon particles are etched by $\mathrm{H}^+$, the reaction product is silicon tetrachloride. The reaction mechanism can be expressed by Eq. (2).

$$\mathrm{Si} + \mathrm{HCl} \longrightarrow \mathrm{SiCl}_4 + 2\mathrm{H}_{2(\mathrm{g})}. \quad (2)$$

As the silicon tetrachloride cannot be removed fast enough, the surface of the silicon particles is covered by this reaction product, which leads to the decrease of the reaction rate. Then the removal rate of the metallic impurities is very slow; especially in a latter stage of the acid leaching. When an ultrasonic field is used during the acid leaching process, the cavitation and acoustic effects of the ultrasonic field enhance the wettability between the metallic impurities and the acid solution, increases the reaction region, improves the reaction conditions, and make the reaction proceed more complete. It should be noted that acid leaching under an ultrasonic field can not avoid the decrease of the acid leaching rate. However, the effects of the ultrasonic field on the particles can break the aggregation of reaction products, which can, therefore, delay the decrease of the removal efficiency. In some situations, the concentration of metallic impurities probably increases, which is due to the formation of insoluble fluorides or other substances[25].

Acid leaching under an ultrasonic field can accelerate the reaction between the impurities and the acid solution. The application of the ultrasonic field during the acid leaching process enhances the reaction efficiency and improves the purifying effect of MG-Si. In a nutshell, HCl leaching under an ultrasonic field can remove the concentration of Fe, Al, and Ti impurities from MG-Si. It is interesting to note that only applying solidification refining once in subsequent metallurgical purification processes can allow the purification of SoG-Si.

## 5. Conclusions

The optimum parameters for acid leaching under an ultrasonic field are: HCl leaching, a particle size of 0.1 mm and a leaching time of 8 h. Using an ultrasonic field in the acid leaching process can improve the purifying effect significantly. As a preliminary process to the metallurgical method, the acid leaching under an ultrasonic field is a more effective method to remove Fe, Al, and Ti impurities comparing to acid leaching using magnetic stirring.

## References

[1] Moller H J, Funke C, Rinio M, et al. Multicrystalline silicon for solar cells. Thin Solid Films, 2005, 487: 179

[2] Goetzberger A, Hebling C, Schock H W. Photovoltaic materials, history, status and outlook. Mater Sci Eng R, 2003, 40: 1

[3] Otubo J, Rigo O D, Neto C M, et al. The effects of vacuum induction melting and electron beam melting techniques on the purity of NiTi shape memory alloys. Mater Sci Eng A, 2006, 438–440: 679

[4] Pires J C S, Otubo J, Braga A F B, et al. The purification of metallurgical grade silicon by electron beam melting. J Mater Process Technol, 2005, 169(1): 16

[5] Arafune K, Ohishi E, Sai H, et al. Directional solidification of polycrystalline silicon ingots by successive relaxation of supercooling method. J Cryst Growth, 2007, 308(1): 5

[6] Kitamura M, Usami N, Sugawara T, et al. Growth of multicrystalline Si with controlled grain boundary configuration by the floating zone technique. J Cryst Growth, 2005, 280: 419

[7] Yokoyama U M. Metal purification method and metal refinement method. Sony Corporation (USA), 2002

[8] Dimassi W, Bouaicha M, Nouri H, et al. Combination of gettering and etching in multicrystalline silicon used in solar cells processing. Nucl Instrum Methods Phys Res B, 2006, 253(1/2): 264

[9] Secco Daragona F, Liaw H M, Heminger D M. Effect of impurity gettering on the efficiency of metallurgical-grade silicon solar cells. Solar Cells, 1983, 10(2): 129

[10] Tucker N P. Preparation of high purity silicon. J Iron Steel Ind, 1927, 15: 412

[11] Voos W. Production of pure silicon. USA Patent, 2 972 521. 1961

[12] Hunt L P, Dosaj V D, McCormick J R, et al. Purification of metallurgical-grade silicon to solar-grade quality. International Symposium on Solar Energy, 1976: 200

[13] Chu T L, Chu S S. Partial purification of metallurgical silicon by acid extraction. J Electrochem Soc, 1983, 130(2): 455

[14] Sakata T, Miki T, Morita K. Removal of iron and titanium in poly-crystalline silicon by acid leaching. J Jpn Inst Met, 2002, 66: 459

[15] Yu Z L, Ma W H, Dai Y N, et al. Removal of iron and aluminum impurities from metallurgical grade-silicon with hydrometallurgical route. Trans Nonferr Met Soc China, 2007, 17: s1030

[16] Henglein A. Sonochemistry: historical developments and modern aspects. Ultrasonics, 1987, 25(1): 6

[17] Mason T J. Current trends in sonochemistry. Ultrasonics Sonochemistry, 1994, 1(2): S133

[18] Gasgnier M, Albert L, Derouet J, et al. Ultrasound effects on various oxides and ceramics: macro- and microscopic analyses. J Solid State Chem, 1995, 115(2): 532

[19] De Azevedo W M, de Oliveira L A J H, Silva E F V B N, et al. The effect of ultrasonic waves in conducting polymer solution. Ultrasonics Sonochemistry, 2006, 13(5): 433

[20] Ashokkumar M, Lee J, Kentish S, et al. Bubbles in an acoustic field: an overview. Ultrasonics Sonochemistry, 2007, 14(4): 470

[21] Ma X D, Zhang J, Wu Y P, et al. Research on hydrometallurgical purification of metallurgical grade silicon under ultrasonic field. J Func Mater, 2008, 39: 1071

[22] Morita K, Miki T. Thermodynamics of solar-grade-silicon refining. Intermetallics, 2003, 11(11/12): 1111

[23] Gasaparini M, Rota F. Crystal growth techniques and segregation effects in solar grade silicon. Mater Chem Phys, 1983, 9(1–3): 79

[24] Eskin G I. Cavitation mechanism of ultrasonic melt degassing. Ultrasonics Sonochemistry, 1995, 2(2): S137

[25] Santos I C, Goncalves A P, Santos C S, et al. Purification of metallurgical grade silicon by acid leaching. Hydrometallurgy, 1990, 23(2/3): 237