Effect of Temperature and Particle Size on the Acid Leaching Process for Solar Grade Silicon Production

Marina Rodrigues de Aguiar, Assistant Professor
Universidade Paulista - UNIP
Paulo Roberto Mei , Professor
Departamento de Engenharia de Materiais
Faculdade de Engenharia Mecânica - UNICAMP
13083- 970 - Campinas - São Paulo- BRAZIL
e-mails: mraguiar@uol.com.br
pmei@fem.unicamp.br

Acid leaching is one of the steps in the production of low cost solar grade silicon from metallurgical grade silicon. The whole process includes directional solidification of silicon to produce polycrystalline ingots that are cut into wafers for solar cells manufacturing. In this paper, we analyze the results of acid leaching on $< 37\mu m$, $74\mu m$, and $105\mu m$ particle sizes of silicon using HCl, HF, and H_2SO_4.. The temperatures used in our experiments were below the boiling point of the acids. As a good illustration of the temperature effects, we have shown the results of the leaching process for two temperatures (25°C and 75°C), and for three different periods of time. Emission spectroscopy of major metallic impurities in silicon, such as Ni, Fe, Mn, Mg, Cu, and Ti, provides the degree of purification under the leaching conditions studied. The best particle size and batch temperature for acid leaching to produce solar grade silicon has been determined.

1. Introduction

Silicon is one of the best materials for photovoltaic applications not only because of its electrical properties and all the advantages of the easily formed oxide layer but also because of its relation with economy, reproducibility and availability for industrial processing. This statement by Dietl (1981) has been often heard by that time. Even though many semiconductor compounds have been developed for photovoltaic conversion, silicon is still the solar cell industry most used material. As Sopori (2002) states, among materials for photovoltaic devices the production silicon has a share of 80%. The photovoltaic energy production is expected to increase more than 70% in MW/yr, from the year 2001 to 2005.

Silicon is generally produced by carbothermal reduction of silicon dioxide, yielding metallurgical grade silicon (MG-Si), about 98% pure. Most of the silicon production is used by steel and aluminum industries, followed by the polymer industries such as silicone production. The smallest part goes to the electronic industry for high purity electronic-grade silicon (EG-Si) processing. Solar cells manufactured from MG-Si would lead to very low photovoltaic conversion efficiency because of the high level of

impurities content. However, solar cells manufactured from EG-Si have high production costs. Many alternative processes that produce solar grade silicon (SG-Si) have been studied. One of these alternative processes for the production of low cost solar cells can be described in three steps. The first step starts with the carbothermal reduction of quartz (Pizzini, 1986), it is followed by acid leaching as a pre-purification process of the MG-Si. The third step involves unidirectional solidification for the production of polycrystalline solar grade silicon ingots. The purity of SG-Si is intermediate between that of the EG-Si and MG-Si. The advantages of these processes are very suitable for a country like Brazil. First of all, it has abundance of high quality quartz what would minimize the raw material cost in the solar cells production chain, and second, its location on Earth, allowing 4000 hours of sunshine per year, while countries outside the tropical region can expect only about 2500 hours Corinna (1981).

Researchers from different parts of the world have also been studying this alternative process in order to minimize costs and increase efficiency of solar cells. Lian et. al. (1992) have shown preference for HCl rather than the more dangerous HF. Margarido et. al. (1993, 1994, 1997) have studied acid leaching and dissolution behavior for some metallic impurities in silicon and silicon-iron alloys. Monamohanan et.al. (1995) have analyzed MG-Si and SG-Si by emission spectroscopy for polysilicon solar cells characterization. Sakata et. al. (2002) have shown their results for removing Fe and Ti by acid leaching of polycrystalline silicon.

This paper discusses the influence of temperature and particle size on the acid leaching step of MG-Si purification.

2. Leaching And Temperature

Leaching is a unit operation that provides for the preferential dissolution of a certain component in a solid mixture by a liquid solvent. It can be applied either for recovering vegetal oils from their seeds or for dissolving impurities in an insoluble solid. Aguiar et.al. (1987) describes acid leaching of silicon as an example of the last application. The theoretical viability of the extraction can be verified through Pourbaix (1974) diagrams, which are based on thermodynamic equilibrium of electrochemical reactions. They are constructed using the potential difference (Volts) versus pH of the solution. Pourbaix diagrams indicate the existing form of a metal, metal ion or metal compound as a function of pH and potential difference. As our interest in this research is to reduce metallic impurities, such as Ni, Fe, Mn, Mg, Cu, and Ti, in silicon by acid leaching, these elements should be in solution for acidic pH values. That is exactly what the Pourbaix diagrams show, enabling us to proceed with the experiments. Solubility tables and Ellingham diagrams have also been employed to help the analysis of the acid leaching performance.
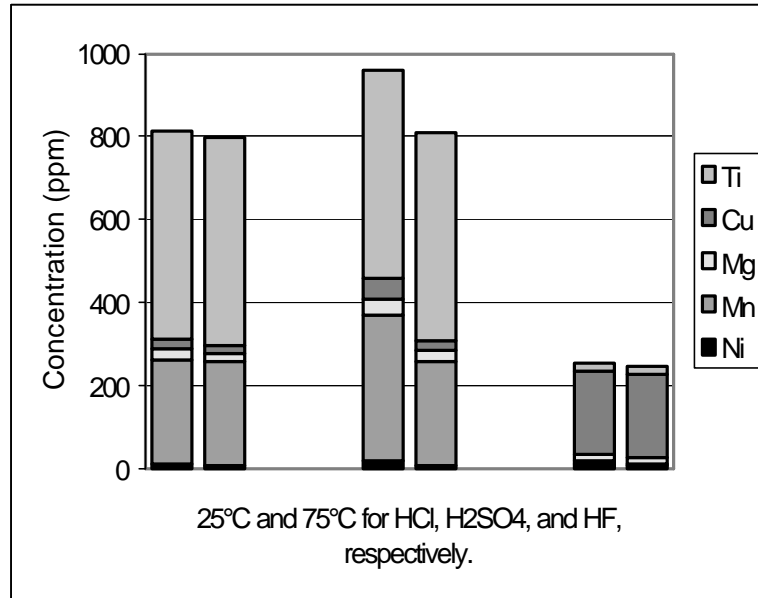
*Figure 1- Effect of temperature on acid leaching of <37 **m**m silicon particles size, for 12 hours. (Acid concentration: 18% w.)*

Particle size, temperature, leaching time, and solvents used are some of the parameters that will determine the velocity and efficiency of the extraction (Treybal, 1980). Fine MG-Si was ground by attrition with different diameters of alunmina balls and screened to separate particles size into < 37µm, 74 µm, and 105 µm. These particles were leached with 18 % by weight hydrochloric acid, hydrofluoric acid, and sulfuric acid at different temperatures and for different periods of time. The leached silicon analysis has carried by emission spectroscopy with carbon electrodes and 10 mg of moisture 1:1 (Si - 8% NaF/ Carbon -600 µg Pd/g). In order to illustrate the temperature effects we have chosen 25°C and 75°C for acid leaching of <37µm silicon particles for 8 hours. Figure 1 shows the results. All the samples were analyzed by emission spectroscopy to determine the percentage of the cited impurities remaining in silicon. The iron concentration is not shown on Figure 1 because the results found greater than 1000 ppm for HCl and H_2SO_4, and about 60 ppm for HF.

In most cases, the material solubility increases with temperature, providing an increase in the extraction rate. Also, the diffusion coefficient increases with temperature. Elevated temperatures usually benefit the leaching process. Our experiments of temperature were limited to the acids boiling point, and have shown that purification results for 75°C were slightly better.

The length of time of phase contact has to be evaluated for each system, and it should be the minimum necessary for maximum extraction, to minimize the operation costs.

Table 1 – Length of time for acid leaching of < 37 μm silicon particles size. (Acid concentration: 18% w. Impurities concentration: ppm)

Acids	Time (hr)	Ni	Mn	Mg	Cu	Ti	Fe
HCl	8	9	250	20	20	500	>1000
	12	9	250	20	20	500	>1000
	24	9	250	15	25	500	>1000
H$_2$SO$_4$	8	9	250	25	25	500	>1000
	12	9	250	20	25	500	>1000
	24	9	250	20	32	500	>1000
HF	8	9	5	15	200	18	60
	12	9	5	12	150	18	36
	24	9	5	12	150	18	36

The results have shown no significant differences in purity for the leaching times using 8 hours, 12 hours, and 24 hours, as can be observed on Table 1. This means that the extraction process has finished before 8 hours. The impurity level for HF decreases when the leaching time increases from 8 to 12 hours, and increases when the leaching time increases from 12 to 24 hours. This could be explained either from the imprecision associated with the analytical technique or the solubility behavior of some metallic compounds impurity in HF.

3. Leaching And Particle Size

The particle size is important in solid-liquid extraction, which is a function of surface area. The porosity and pore distribution can strongly affect the extraction rate because the leaching solution in the solid flows into and out of the pores. In many cases the solute movement through the pores to the surface is by diffusion. Usually, reduction of the particle size will reduce the residence time of the dissolved solute molecules inside the particle (Treybal, 1980).

On the other hand, very finely sized particles will lead to the formation of agglomerates. Figure 2 shows the results for the acid leaching of three different particle sizes. In a previous work (Aguiar, 1989), it was demonstrated that a particle size <37μm exhibit agglomeration, and hence is more difficult to handle. Actually, for sulfuric and hydrofluoric acids the best size was 74μm while for HCl, 105μm was the best, showing that there must be a relation between particle size and acid type.Table 2 shows the concentration results for Fe after acid leaching of different particle sizes of silicon. Again, the remaining metallic concentration differences varies from 30 ppm to 1000 ppm depending on the type of acid used.

Solubility charts (Perry, 1990) show that certain metallic compounds are soluble in acids in general, while others will dissolve only by specific acids. So, some metals and their compounds can be soluble in an acid A and insoluble in acid B , even if acids A and B are of the same class. For example, CuO$_2$ is soluble in HCl, CuO is soluble in acids in general, and copper is insoluble in HF. Examining Table 1 data for copper behavior after acid leaching, it shows that there was more copper remaining in silicon when HF was used. On the other hand, only HF was able to remove Fe.
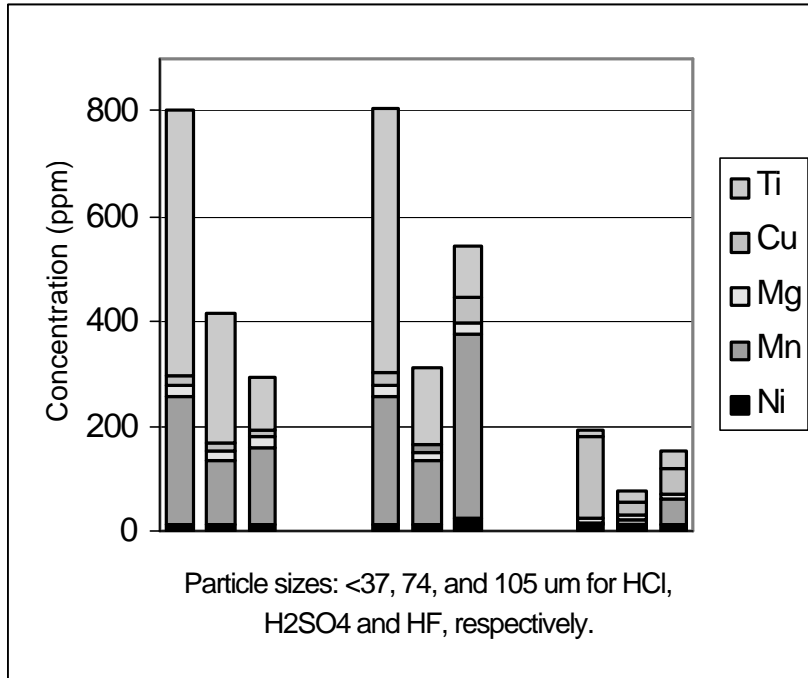
*Figure 2 – Effect of particle size (<37, 74, and 105 m*m*) on acid leaching for 12 hours each, at 75°C. (Acids concentration: 18% w.)*

Table 2 - Effect of particle size (<37, 74, and 105 μm) on acid leaching for 12 hours each, at 75°C, on Fe impurity. (Acids concentration: 18% w.)

Acids	Particle size (μm)	Fe
	37	>1000
HCl	74	>1000
	105	800
	37	>1000
H_2SO_4	74	1000
	105	1000
	37	36
HF	74	80
	105	500

4. Conclusions

The temperatures (25 and 75°C) and the periods of time (8, 12 and 24 hours) did not influence significantly the results of leaching. The particle sizes (>37μm, 74μm, and 105μm) and types of acid used (HCl, HF, and H_2SO_4) have shown a palpable influence on the leaching. The best parameters found in our experiments for acid leaching of silicon were 74μm for HF and H_2SO_4, and 105 μm for HCl; 75°C as batch temperature;

8 hours for HCl and 12 hours for HF, and H_2SO_4. We have started with 98% pure MG-Si. After acid leaching we have reached approximately 99,8% pure silicon.

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