Upgraded Silicon Via Acid Leaching

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ABSTRACT

A 99% purer metallurgical silicon can be obtained from reduction of quartz with Brazil's charcoal used as a carbon source. The high purity metallurgical grade silicon obtained so is used as starting material for the acid leaching process and later unidirectional solidification, for producing polycrystalline ingots. This is a possible route for obtaining low cost and pure enough silicon to fabricate terrestrial photovoltaic devices. In this work it is focused the studies made toward optimization of acid leaching process. The effects of leaching parameters such as temperature, time, type and concentration of acids are analysed in function of particules size (< 37 to 100 µm). The leached, washed and dried silicon is then analysed for major impurities by emission spectroscopy. The results of this investigation are reported and discussed in this paper.

1. INTRODUCTION

Silicon solar cells are usually manufactured from wafers cut from single or polycrystalline semiconductor-grade silicon (SeG-Si) ingots. The SeG-Si can be obtained by using the well-established Siemens C process, which involves high cost steps.

Since silicon purity requirements for photovoltaic cells for terrestrial applications are smaller than for the SeG-Si, much attention has been focused on upgrading the metallurgical-grade silicon (MG-Si) in order to reduce the cost of solar cells.

Charcoal, commercially used as a reductant for quartz in Brazil, has been shown to be of higher purity in most trace elements than commercial reductants commonly used overseas.[1]

This means that more than 99% pure MG-Si can be obtained by carbothermic process:

$$SiO_2(s) + 2C\ (s) \overset{\Delta}{\rightarrow} \underset{MG-Si}{\underline{Si\ (\ell)}} + 2CO\ (g)$$

The high purity MG-Si obtained so can be upgraded by several chemical and physical techniques.

A potential route to silicon for solar cells involves an acid leaching of the MG-Si to produce a material of sufficient quality to be directionally solidified. As a result an ingot called solar-grade silicon (SoG-Si) can be obtained and then cut into wafers for solar cells fabrication.

This work is concerned with studies using acid mixtures such as acqua regia and HF/H_2SO_4 for the acid leaching.

2. ACID LEACHING

Mass transfer operations are characterized by the transfer of a substance from one environment to another on a molecular scale.

Solid-liquid extraction is one of the mass transfer operations which involves dissolution of one or more components from one solid solution to another liquid solvent. This can occur by chemical reaction or by simple solution.|2| One of the well-known solid-liquid extraction is leaching.

Leaching may be used either for producing a concentrate valuable substance such as vegetables oils from seeds, gold from its ores, or for making an insoluble solid free from many impurities. This is the case of the silicon leaching.

Generally, the extraction process can be divided into three parts: first, the solute phase changes when it is dissolved by the solvent; second, the solute diffusion while in the solvent will extract the particle through the solid porous; and finally the transfer of the solute from the solution around the particle to the bulk of the solution. Any of these steps may limit the extraction rate. Although the first step generally occurs so fast that it may be unnoticeable in the total rate.

The factors that may act on efficiency of the extraction rate are:

1. Particle size
2. Solvent and solvent temperature
3. Agitation of the bath
4. Length of time for leaching

2.1 Particle Size

Particle size may influence the extraction rate in many ways. The smaller the particle size, bigger the interface area between the solid and the liquid, shorter the distance the solute has to diffuse inside the solid and consequently higher the transfer rate of the material.

2.2 Solvent and Solvent Temperature

The chosen liquid must be a selective solvent and its viscosity must be low enough to make it free to move. In most cases, an increase in the solvent temperature can lead to an increase in the solute solubility and a decrease in the solvent viscosity. The matrixes must not be solubilized.

2.3 Agitation of the Bath

The bath agitation improves the solid-liquid interfacial surface use. It provides a change in the impurities concentration gradients of the liquid phase that can rise the extraction rates.

2.4 Length of Time for Leaching

For a set of conditions, the length of time for extraction must be long enough to able the maximum solute solubilization from the solid matrix.

For predicting if a particular reaction will proceed under a given set of extraction conditions, some properties such as solubilities, activity coefficients, equilibrium constants, etc., can be determined by thermodynamics calculations.

The electrochemical or the chemical equilibrium |3| relationships of species that make up a given system can be represented in two-dimensional plots. The potential-pH diagrams, known as diagrams of Pourbaix, are of that kind.|4| At zero potential in these diagrams we can obtain some

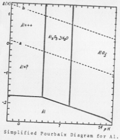

Figure 1 - Simplified Pourbaix Diagram for Al.

information about chemical equilibrium such as the necessary pH for solubilizing the analysed element.

The simplified Pourbaix diagrams for Al, Fe, Mg, Mn and Ni are exhibited below (Figures 1 to 5, respectively), showing that for acids pH at zero potential, these elements can be in solution.

3. EMISSION SPECTROSCOPY ANALYSES

Since we had many experienced samples, emission spectroscopy had been used to analyse silicon because it is available at a reasonable cost and provides a fast multielement analyses.

This method of analyse cannot provide reliable data for certain silicon impurities such as boron and phosphorus. But many metal impurities analysed by emission spectroscopy can yield realiable data. Much attention must be given with regard to the determination of small changes in impurity |5| levels. In this case, emission spectroscopy can provide misleading data. Although emission spectroscopy reliability is good enough for our inicial purposes.

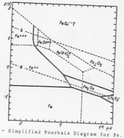

Figure 2 - Simplified Pourbaix Diagram for Fe.

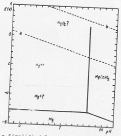

Figure 3 - Simplified Pourbaix Diagram for Mg.

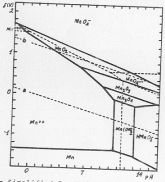

Figure 4 - Simplified Pourbaix Diagram for Mn.

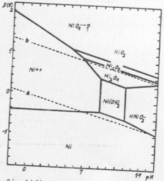

Figure 5 - Simplified Pourbaix Diagram for Ni.

4. RESULTS

The approximate impurities level of MG-Si before leaching is shown in Table 1.

The MG-Si particles of 74 μm and 37 μm size were leached, for the same period, by a mixture of HF/H_2SO_4 at |6| 80°C. After leaching, the washed and dried silicon was analysed by emission spectroscopy and the results are shown in Table 2. It can be observed that for smaller particles, in this procedure, the leaching was 27% more efficient than for 100 μm particles.

Table 3 and Table 4 show the extraction results of 37 μm MG-Si by acqua regia and a mixture of HF/H_2SO_4 respectively, at both temperature, 20°C and 80°C. In the acqua regia leaching, with and increase in the temperature there can occur an increase of 5% in the approximate total of the impurities removal, while in the case of HF/H_2SO_4 mixture the increase of removal is around 15%.

The results of Tables 3 and 4 suggest that a combination of many acids or acid mixtures can yield a purer silicon. For instance, the acqua regia can reduce by 20% the level of Mn and by 89% the level of Cu while with HF/H_2SO_4 there can be obtained a reduction of 98% for Mn and no reduction for copper.

In a previous atomic absorption spectroscopy analyse the V level was not detectable. Here, it must be noted that Ti level can be effectively reduced (more than 96%). These are very good results since Ti and V are two of the solar cells lifetime killers.|5|

5. CONCLUSIONS

Based upon the informations presented above, it seems that a smaller cost SoG-Si process can be developed.

The results have showed that this low-cost metallurgical procedure can decrease the total amount of impurities from about one order of magnitude.

Solar cells produced from only moderately purified MG-Si showed approximately 4% conversion efficiency. This result suggests that improved MG-Si purification can yield higher efficiency solar cells.

Impurity	MG-Si (ppm)
Fe	> 1000
Ni	∿ 20
Al	> 500
Mn	> 250
Mg	∿ 50
Cu	∿ 140
Ti	> 500

Table 1 - MG-Si before leaching

Impurity	74 μm (ppm)	(%) app. removal	100 μm (ppm)	(%) app. removal
Fe	∿ 60	94	∿ 100	90
Ni	< 9	55	< 9	55
Al	∿ 100	80	∿ 500	-
Mn	∿ 9	96	∿ 25	90
Mg	< 12	76	< 12	76
Cu	∿ 25	82	∿ 50	64
Ti	∿ 70	86	∿ 250	50

Table 2 - Leaching of 74 μm and 100 μm MG-Si with HF/H_2SO_4 at 80°C.

Impurity	20°C (ppm)	(%) app. removal	80°C (ppm)	(%) app. removal
Fe	> 1000	-	> 1000	-
Ni	∿ 12	40	< 9	55
Al	> 500	-	> 500	-
Mn	> 250	-	∿ 200	20
Mg	∿ 25	50	∿ 25	50
Cu	∿ 50	64	∿ 15	89
Ti	∿ 400	20	∿ 350	30

Table 3 - Leaching of 37 μm MG-Si with acqua regia at 20°C and 80°C.

Impurity	20°C (ppm)	(%) app. removal	80°C (ppm)	(%) app. removal
Fe	∿ 60	94	< 36	96
Ni	< 9	55	< 9	55
Al	∿ 400	20	∿ 100	80
Mn	< 4,5	98	< 4,5	98
Mg	< 12	76	< 12	76
Cu	∿ 200	-	∿ 150	-
Ti	∿ 18	96	∿ 18	96

Table 4 - Leaching of 37 μm MG-Si with HF/H_2SO_4 at 20°C and 80°C.

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