

## LOW-COST PURIFICATION OF METALLURGICAL SILICON FOR PHOTOVOLTAIC APPLICATION

التنقية منخفضة التكاليف للسيليكون المتالورجى  
للاستخدام الفوتوفولتائى

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الخلاصة - تم اسحداثا طسية جديدة منخفضة التكاليف لاعداد السيليكون القمى الدرجة والمبني على المعالجة بالاحماض والاستخلاص بقماسى اكسيد الفوسفور عند درجة الحرارة المرطعة للسيليكون المتالورجى الدرجة وذلك لازالة الشوائب المعدنية الضارة. والمادة المبتدا بها هي السيليكون المتالورجى المسحوق. ونحصل على التنقية بواسطة الغلى المعلق المسحمر للسيليكون مع مخلوط من الاحماض لمدة حوالى 14 يوما، مع استبدال الحامض بمخلوط طازج كل حوالى 3-5 ايام. وهم تحديد محتوى الحديد فى السيليكون والهامض المسحمر باستخدام طريقة سيكتروفوتومترية. ولد وجد ان المعالجة بالهامض تكون فعالة جدا فى خفض محتوى السيليكون من الشوائب المعدنية الضارة. ثم استخدم الاستخلاص بقماسى اكسيد الفوسفور للحصول على تنقية اعلى للسيليكون المعالج بالاحماض. كونت عجينة كثيفة من السيليكون المعالج بالحمض و 5% بالوزن من قماسى اكسيد السيليكون و الماء المزال الايونات، و سفنت العجينة عند 1050 1.5م لمدة أربعة ايام فى وعاء نظيف من الكوارتز فى الهواء. و عولجت الشحنة الناتجة بقمض الهيدروفلوريك لازالة الزجاج الفوسفوسيليكاسى المحكون ثم نظفت و عولجت بالماء الملحى لعدة ايام. ولد ادى ذلك الى انخفاض محتوى السيلكون من الحديد الى 150 - 250 ج.ف.م. ولد استخدمنا السيليكون المعالج بالحمض والمستخلص لانتاج طبقات تمتية كبيرة المساحة وذلك باستخدام الصهر ثم التصليد فى اتجاه واحد، للاستخدام فى عمل خلايا شمسية. وضانت المقاومة النوعية 0.3 اوم.سم وضادت من النوع السالب، مما يجعلها مناسبة جدا لتصنيع الخلايا الشمسية.

**Abstract :** A new, simple, low-cost technique for the preparation of solar-grade silicon, based on acid-treatment and high-temperature phosphorus-pentoxide gettering of metallurgical-grade silicon for removing the harmful metallic impurities is reported. The starting material is pulverized metallurgical-grade silicon. Purification is achieved by continuously boiling the silicon in a mixture of acids under reflux conditions for about 14 days, replacing the acid by a fresh mixture every 3-5 days. Iron content in the silicon and in the extracted acids was determined using a spectrophotometric technique. Acid leaching was found to be effective in appreciably reducing the content of harmful metallic impurities. Gettering with phosphorus pentoxide was used to achieve further purification of the acid-treated silicon. A thick paste of the acid-leached silicon, 5% by weight of phosphorus pentoxide and de-ionized water was heated at 1050 °C for 4 days in a clean quartz container in air. The resulting charge was treated with hydrofluoric acid to remove the phosphosilicate glass, and then cleaned and refluxed with aqua regia for several days. The iron content in the silicon was further reduced to 150 - 250 ppm. The acid-leached and gettered silicon was used to produce a large area substrate using melting and unidirectional solidification, for solar cell fabrication. The substrate had a resistivity of 0.03 Ω.cm and was n-type, making it very suitable for solar cell fabrication.

## INTRODUCTION

Semiconductor-grade silicon is too expensive to be used for the fabrication of solar cells for terrestrial use. Metallurgical-grade silicon (MG-Si) has a purity of about 98%, and is not suitable for photovoltaic applications. Several techniques have been reported for the production of "solar-grade" silicon from MG-silicon [1], including treatment of molten silicon by chlorine or oxygen [2], casting and controlled cooling [3,4], solvent refining [5], Czochralski crystal growth [6,4] and combined chemical treatment and unidirectional solidification [7,8].

MG-silicon is produced for use in steel and aluminum industries by the carbon reduction of quartzite in an arc furnace. It is sold in the form of chunks containing about 98% silicon. Table (1) shows some of the typical impurities in MG silicon and their equilibrium segregation coefficient. Metallic impurities have segregation coefficients that are much smaller than unity. Transition metal impurities, such as iron, aluminum, nickel and copper are the most harmful impurities in MG-silicon, and they are known to significantly reduce the minority carrier lifetime in single crystalline silicon. These impurities, are highly soluble in liquid silicon [9], thus they mainly accumulate at grain boundaries in the form of silicides and other compounds during the solidification of molten MG silicon.

TABLE (1) Typical impurities in MG-silicon

| Impurity                            | Al                 | B                    | Cr                   | Cu                   | Fe                   | Mg                   | Mn                   | Ni                   | Ti                   |
|-------------------------------------|--------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| Concentration (ppm)                 | 650                | 10                   | 11                   | 10                   | 1500                 | 0.5                  | 40                   | 25                   | --                   |
| Equilibrium segregation coefficient | $3 \times 10^{-2}$ | $1.1 \times 10^{-5}$ | $1.1 \times 10^{-5}$ | $6.4 \times 10^{-6}$ | $6.4 \times 10^{-6}$ | $3.2 \times 10^{-6}$ | $1.3 \times 10^{-5}$ | $2.0 \times 10^{-6}$ | $2.0 \times 10^{-6}$ |

The pulverization of the cast MG-silicon takes place at the grain boundaries, therefore the treatment of the pulverized MG silicon with acids should remove a large percent of these impurities, and it was reported that 90% of all impurities except boron, copper and phosphorus could be removed from MG

silicon by acid treatment [10], and the treatment of pulverized MG silicon with aqua-regia, sulphuric acid, ... etc., produced silicon suitable for microwave devices [11]. The effectiveness of acid treatment should be increased by crushing the MG silicon lumps to a size comparable to the size of the individual polycrystalline grains. Recently, the preparation of silicon ribbons from acid-leached metallurgical silicon by a powder-to-ribbon process [12], and by unidirectional solidification [13,14] has been reported.

Gettering techniques using phosphorus pentoxide were found effective in removing metallic impurities in single crystalline silicon [15-17].

#### ACID-LEACHING OF MG-SILICON

Pulverized metallurgical-grade (MG) silicon, purchased from Union Carbide Co. was the starting material. The nominal size was 30 - 80 mesh (0.3 - 0.8 mm), and the nominal iron concentration in the MG-silicon was 0.34%. The MG silicon was sieved using a 0.3 x 0.5 mm metal grid. In a typical run out of 2680 g of MG silicon, 2110 g were > 0.3 mm. About 2 kg of MG silicon were put in a 3-l pyrex flask, and 1.2 l of acid were added. Heating was started, under reflux conditions, and continued for 5-7 days. The acid changed color (to brownish yellow). The acid solution was replaced by a fresh solution, the silicon was rinsed with de-ionized water, and then heating was continued. The process was repeated several times until the acid solution was colorless. This usually took 4 - 5 acid replacements. Various acid solutions were tested: aqua-regia, hydrochloric acid, and a 1 : 1 (volume) sulphuric-nitric acids. The concentration of iron was measured in the starting MG silicon, in the acid-treated silicon, and in the extracted acid solutions, using the spectrophotometric technique explained in the next section.

#### Measurement of Iron Concentration

A spectrophotometric technique was used to determine the iron content in the treated silicon and in the extracted acid. Ferrous ions in aqueous solutions are known to form colored complexes with a number of organic reagents, and the concentration of iron in a solution can be determined by measuring the peak of the absorption of these complexes in the visible region. (1,10)-phenanthroline ( $C_{12}N_2H_8$ ) was used as complex agent for the quantitative determination of small

concentrations of iron in solutions [18].

In order to apply this technique, a weighed amount of the acid-treated silicon was dissolved in an ammonium fluoride-nitric acid mixture (20 g of  $\text{NH}_4\text{F}$  in 100 ml of 70%  $\text{HNO}_3$ ). The solution was then neutralized using ammonia, and the pH was adjusted to 2-2.5. Five ml of an aqueous solution of hydroxylamine hydrochloride (10% by weight) was then added to the solution to reduce the ferric ions to the ferrous state. Then 15 ml of an aqueous solution of (1,10)-phenanthroline (0.3% by weight) were added to form the colored complex (15 ml insures that an excess of the complexing agent is present). The color did not develop until the pH of the solution became 6.5. The solution was then diluted in de-ionized water and the optical absorption was measured at a wavelength of 510 nm. Figure (1) shows the optical absorption curve of the complex formed by the ferrous ions and (1,10)-phenanthroline, determined using a 1x1 cm standard cell, using a Varian Cary 118 instrument. It is noticed that the curve has a peak at a wavelength of 510 nm. The height of this peak is linearly proportional to the intensity of the iron in the solution, as was verified by preparing a set of "standard" solutions of known iron concentrations. Figure (2) shows the percentage optical absorption vs iron concentration in the standard solutions.

#### Phosphorous-Pentoxide Gettering

The acid-treated silicon was mixed with 5% (by weight)  $\text{P}_2\text{O}_5$  and de-ionized water, forming a thick paste, which was loaded into a clean quartz container and heated in air at 70 - 100 °C for about 16 Hrs until water vaporized and a solid piece was formed, then the temperature was linearly increased to 1050 °C at a rate of 100 °C per 24 Hrs, and then kept at 1050 °C for 4 days. The resulting charge was treated with diluted HF acid to remove the phosphosilicate glass, and then refluxed with aqua-regia for several days. After that the silicon was thoroughly cleaned with de-ionized water and dried.

#### Silicon Substrate Preparation

Large-area rectangular silicon substrates were prepared from the acid-leached and gettered silicon. 20 - 30 g of the pulverized silicon was uniformly spread on the top of a 15x5 cm graphite plate. The surface of the graphite plate was roughened by sand-blasting in order to hold the silicon when it melts. Unidirectional solidification was used to produce

large-grain silicon substrates suitable for solar cell fabrication by chemical vapor deposition [19]. The silicon was first melted in a high purity hydrogen atmosphere, using rf heating, and then the input power was gradually reduced, and the  $H_2$  increased to start solidification of the silicon at the silicon surface, rather than at the silicon-graphite interface, to minimize the effect of the graphite plate on the grain structure of the silicon substrate, and to yield a columnar structure. Solidification progressed from one end of the graphite plate towards the other end, until all the silicon solidified.

#### RESULTS

Figure (3) shows the iron concentration in the extracted solution, for aqua-regia and sulphuric-nitric mixture, as a function of the extract number. It is clear that aqua-regia is far more effective than the sulphuric-nitric mixture, and that for both cases maximum possible purification is achieved by the third extract. In order to help the remaining heavy-metal impurities in the silicon grains diffuse to the surface the acid-treated silicon was annealed at high temperature (1000 °C) in a high-purity hydrogen atmosphere (flow of 3 l/min) for about 120 Hrs, and then slowly cooled to room temperature. The iron content in the silicon was further reduced, as is clear from figure (4), which shows the iron concentration in the acid-treated, annealed, and gettered silicon. Iron was reduced from 3969 ppm in the starting MG silicon to 1337 ppm after acid-leaching and to 539 ppm after gettering for sample (AL-9), treated with HCl and aqua-regia; to 1704 ppm after acid-leaching and annealing, and to 785 ppm after gettering once (8 hrs) and to 387 ppm after a second gettering process (66 hrs), for sample (Al-8), treated with HCl.

The acid-leached and gettered silicon was used to produce a silicon substrate on graphite by melting and unidirectional solidification. The solidification rate was found to be the factor that determines the morphology of the silicon substrate; high solidification rates (4-5 cm/min) resulted in a non-planar silicon surface, with ridges and valleys, while lower solidification rates (0.5-1.0 cm/min) gave a smooth planar surface. The typical grain size was several millimeters in width and up to several centimeters in length. It was noticed that when a lower purity silicon was used a lot of junk accumulated on the surface of molten silicon and the grain size was usually smaller. The resulting substrate was 0.015  $\Omega$ .cm, n-type, for substrates prepared on graphite from the twice-gettered sample

(AL-8), and 0.03- 0.10  $\Omega$ .cm p-type for an aqua-regia treated-only, sample (AL-10), compared with 0.3  $\Omega$ .cm p-type for substrates prepared from semiconductor-grade silicon (undoped), as was measured by the spreading resistance technique. Iron concentration was also measured as a function of position in the unidirectionally-solidified silicon substrates using same spectrophotometric technique. The result for a planar and a non-planar substrate is shown in figure (5). The substrates were prepared by melting and unidirectional solidification of 18g of acid-treated silicon (sample AL-9) and 0.2g 1% B-doped semiconductor-grade silicon on a graphite plate. A sketch of the morphology of the substrates is shown in figure (6). The substrates were saw cut along the lines shown in the figure. The Roman numerals indicate the samples analyzed for iron content. It is concluded from figure (5) that the higher iron concentration compared to the starting silicon is probably to out-diffusion of impurities from the graphite plate during substrate preparation.

#### CONCLUSIONS

A cost-effective technique is reported for the purification of metallurgical-grade silicon for solar cell application using acid treatment and phosphorus-pentoxide gettering. The technique is simple and cheap, and was used to produce rectangular polycrystalline silicon substrates on graphite by the unidirectional solidification technique. These substrates are suitable for the fabrication of p-n junction solar cells using chemical vapor deposition.

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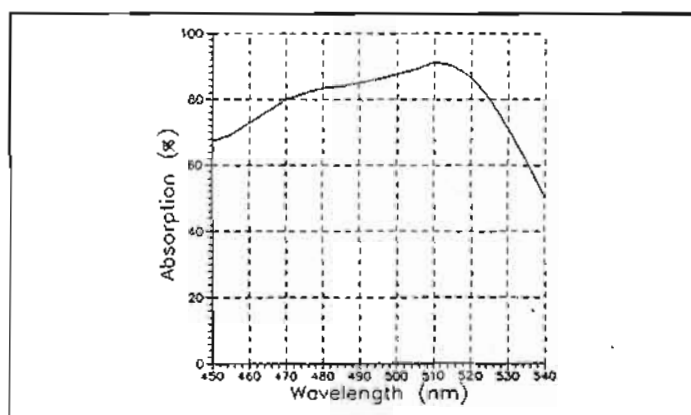


Fig. 1. The optical absorption curve of the complex formed by ferrous ion and (1,10)-phenanthroline



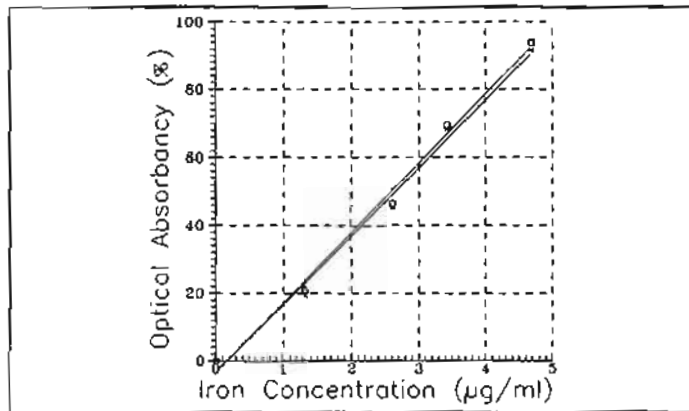


Fig. 2. Percentage optical absorption vs. iron concentration in "standard" solutions

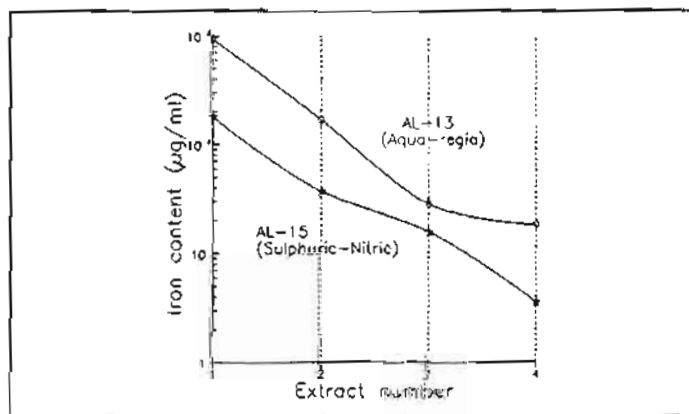


Figure 3. Iron concentration in the extracted solution vs. extract number

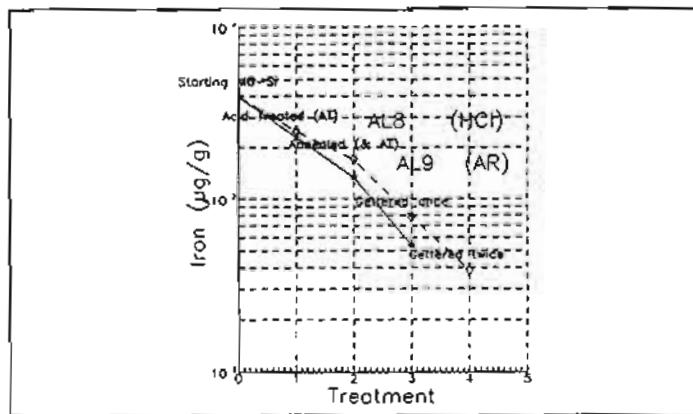


Fig. 4. Iron concentration in the silicon as a function of treatment

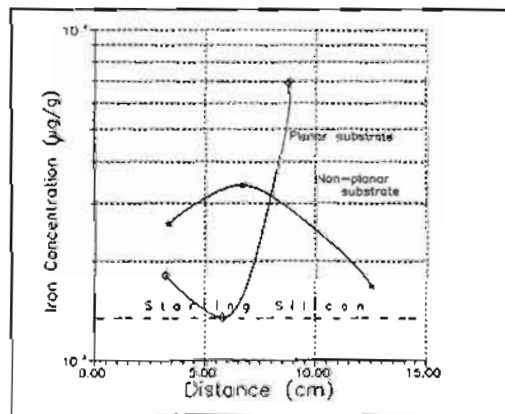


Fig. 5. Iron concentration vs position in planar and non-planar polycrystalline silicon substrates

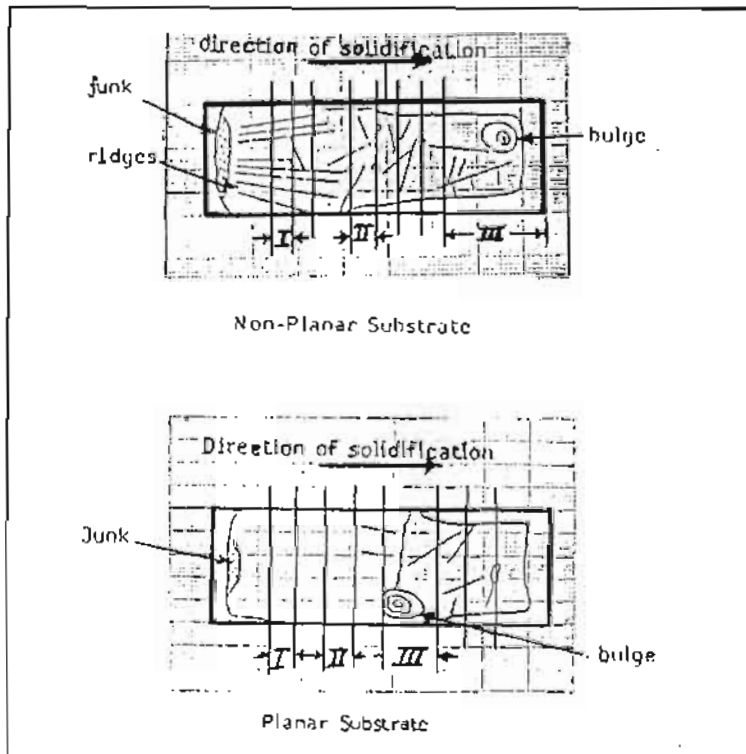


Fig. 6. Morphology of the planar and non-planar polycrystalline silicon substrates