EFFECTS OF IMPURITIES CONCENTRATION ON THE EFFICIENCY OF SOLAR CELLS MANUFACTURED WITH UPGRADE METALLURGICAL SILICON

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ABSTRACT

In this work we reported the production of upgraded metallurgical grade silicon using a combination of different purification techniques, i.e., vacuum degassing, directional solidification and Czochralski growth. Chemical composition, resistivity and efficiency of silicon solar cells are presented. It was observed that those methods have different purification efficiency for different elements. The use of vacuum degassing is demonstrated to be a potential procedure to be used in a combination with other techniques to reduce impurities in metallurgical silicon as well as reduce the final price of the silicon wafers. The combination of vacuum degassing and Czochralski method provided upgraded metallurgical grade silicon. Solar cells efficiency approaching 10% was obtained using this material.

INTRODUCTION

Great efforts has been made to replace conventional electronic grade silicon (EG-Si), purified by the Siemens process, for a less pure silicon developed by a cheaper purification technique, but with purity sufficient to provide solar cell with reasonable high efficiency, the so-called “solar grade silicon”. In this concern, upgrade metallurgical grade silicon (UMG-Si) has been considered as a good alternative. Different purification techniques or combinations of these techniques have been investigated, aiming to reduce the final cost of solar cells [1-4]. UMG-Si usually contains a large amount of boron (B) and phosphorus (P), because they are difficult to be removed, such that the UMG-Si is often compensated [5]. Other metal contaminants such as iron (Fe), nickel (Ni), titanium (Ti) and copper (Cu), introduce deep states, which acts as recombination centers, reducing the carrier diffusion length, mobility and lifetime [6-9]. In this work in investigate the use of a combination of different purification techniques to achieve solar grade silicon.

EXPERIMENTAL DETAILS

Three different techniques were used for the purification of metallurgical grade silicon, i.e., vacuum degassing (VD), directional solidification (DS) and Czochralski (CZ). The vacuum degassing (VD) technique was realized in an electron-beam system, model EMO-LEW. In this technique, static melted silicon is allowed to rest in a vacuum chamber for 30 minutes, favoring the degassing of impurities with high vapor pressures. The base pressure of the system was 10^{-2} Pa. A directional solidification system, with RF frequency source of 9600 Hz and 25 kW, was used. The material was melted in a graphite crucible and an ingot with 15 cm length and 10 cm diameter was grown. Two Czochralski systems, CZ1 and CZ2, were used for the fabrication of crystalline silicon wafers. The CZ1 is a commercial system used for the production of silicon wafers. The CZ2 is a laboratory system, Ther-Monic, model G-2500, with an induction heating furnace using a 250 kHz frequency power supply and 25 kW. Table 1 shows the purification processes and resistivity achieved after the purification using a combination of two techniques. Commercial, electronic grade silicon wafers, from Wacker, CEMAT, and Heliodinâmica were used for comparison.

Conventional p-n homojunction silicon solar cells were fabricated through thermal diffusion of phosphorous (using $POCl_3$ dopant carrier). Gettering process, using phosphorous diffusion, was adopted to further improve the performance of the solar cells. The contacts were performed using an aluminum back surface field, followed by evaporation of metal contacts, a combination of Ti/Pd/Ag. Tin dioxide (SnO_2) antireflective coating was deposited by the spray pyrolysis. The photovoltaic parameters (efficiency, open circuit voltage, short circuit current and fill factor) were determined from current (I) vs. voltage (V) curves using a solar simulator.

Table 1: Description of the silicon wafers and the purification processes used in this work.

Sample	Name	Resistivity [ohm cm]
Wacker – CZ growth	EG-Wa	1,56
Float Zone – FZ growth	EG-FZ	0,55
Cemat – CZ growth	EG-Ce	0,81
Heliodinâmica – CZ growth	EG-He	1,33
Vacuum Degassing (VD)	UMG-Si VD	0,06
Vacuum Degassing (VD) and CZ growth	UMG-Si (VD:CZ2)	0,15
CZ growth (successive CZ growth - commercial system)	UMG-Si CZ1	0,08
Vacuum Degassing (VD) and CZ growth (successive CZ growth - commercial system)	UMG-Si (VD:CZ1)	0,30
Vacuum Degassing (VD) and direction solidification (DS)	UMG-Si (VD:SD)	0,02

RESULTS AND DISCUSSION

a) Chemical analysis by GDMS

Figure 1 shows the results for the chemical analysis realized by GDMS (Glow Discharge Mass Spectroscopy) of the upgraded silicon compared with the starting metallurgical silicon. The vacuum degassing (VD) technique provided a considerable reduction in the concentration of impurities (sample UMG-Si VD), being effective for reducing P, Ti, Fe and Al impurities. Even though the VD is efficient to reduce some impurities, it also evaporates silicon. Thus, it cannot be adopted for a long period of time.

The best result obtained in this work corresponds to the sample prepared by the combination of vacuum degassing and CZ growth (UMG-Si (VD:CZ2)), which provided a material with 5.7 ppm of impurities concentration (99.9994% purity). Thus, the CZ technique was also effective to reduce impurities. In this process segregation and degassing of some impurities are observed. The reduction of B is not due to a segregation process, but to a reaction with oxygen, resulting in BO, B_2O, BO_2, B_2O_3 during the CZ process. This route was effective in reducing the concentration of all impurities.

The use of a combination of VD and multiple steps of CZ growth (sample UMG-Si (VD:CZ1)) presented an inferior performance. Probably, the measured sample was not taken from the purer region of the ingot. We expect a much better performance of this combination. Further work is currently under way to better explore this combination, since it appears to be promising. The effort to replace some of the CZ steps by the VD technique is because the latter is a cheaper technique, since it requires a simpler experimental apparatus and also requires less processing time compared to the CZ technique.

The combination of vacuum degassing (VD) and directional solidification (DS) (sample UMG-Si (VD:DS)) was not effective reducing the impurities.

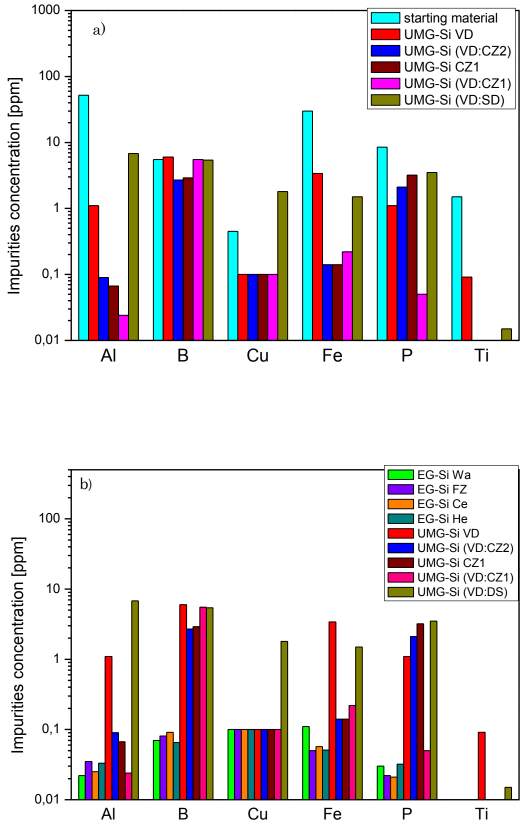

Figure 1: (a) Chemical analysis of the sample purified by metallurgical route and (b) the samples used for the fabrication of solar cells.

Figure 1(b) presents the results of chemical analysis of the electronic grade silicon (EG-Si) and of the upgraded metallurgical grade silicon (UMG-Si) used for the manufacture of solar cells. It is observed that the concentration of B and P in the UMG-Si samples is about 100 times the concentration found in EG-Si samples.

Figure 2 presents the results of chemical analysis of the sample UMG-Si (VD:CZ2) compared with the result reported by Warabisako et al. [1], who performed two consecutive CZ growth using metallurgical grade silicon. The recommended maximum impurity concentration for solar cell application is also included, following the work by Morita and Miki [10]. One can observe that the impurities concentration obtained for the UMG-Si (VD:CZ2) sample is better than that reported by Warabisako et al., but still higher than the values recommended by Morita and Miki. Further improvement is necessary to achieve higher purity. This can be partially accomplished by increasing the time of the vacuum degassing process, since it is an efficient process to remove most to the contaminants, except boron. However, this procedure may not be recommended, considering economic issues. Concerning the reduction of boron, it is necessary to adopt a different approach since none of the process adopted here is good to remove boron.

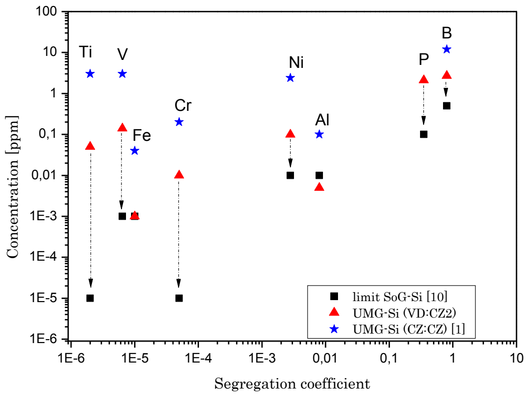

Figure 2: Concentration of impurities of the UMG-Si (VD:CZ2) sample compared with the result reported by Warabisako et al.[1], and the values recommended for solar grade silicon, Morita and Miki [10].

b) Resistivity of upgraded metallurgical grade silicon

Figure 3(a) shows a graph of the resistivity versus the total concentration of impurities. It can be observed that the lower the concentration of impurities the higher is the resistivity, as expected. Figure 3(b) and 3(c) show the resistivity as a function of the concentration of boron and phosphorous, respectively. One observes that the resistivity is mainly determined by the concentration of boron. The contribution of the other impurities does not affect much the resistivity. However, they contribute to create defects that reduce significantly the efficiency of the solar cells.

c) Efficiency of solar cells made with upgraded metallurgical grade silicon

Figure 4(a) displays the efficiency of the solar cells versus the total concentration of impurities. Among the metallurgical routes, it is observed that the sample UMG-Si (VD:CZ1), gave the best result (efficiency of 9,7%). The efficiency of this cell was limited by the high concentration of B as well as P.

The use of a gettering process was effective in removing some impurities and shows itself as an alternative to provide higher efficiency levels in crystalline silicon solar cells manufactured with metallurgical grade silicon.

Figure 4(b) shows the conversion efficiency as a function of the boron concentration. It is noted that the lower the concentration of boron the higher the solar cell efficiency. This is likely to be related to the solar cell fabrication process, which was optimized for silicon with resistivity of about 1 ohm.cm.

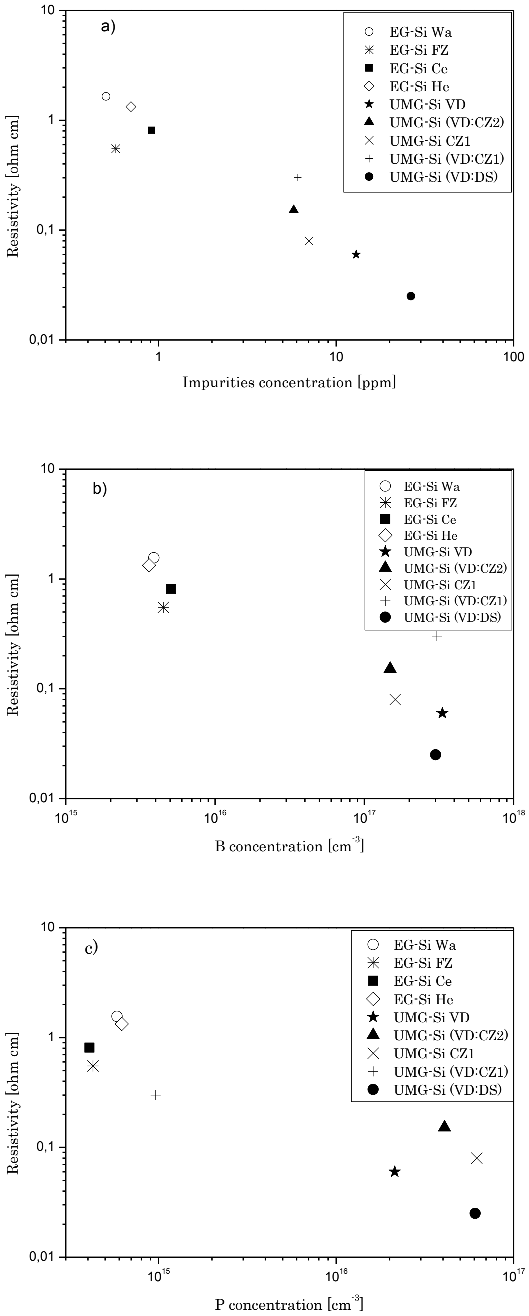

Figure 3: Resistivity of the silicon wafers as a function of the total concentration of impurities (a), boron (b) and phosphorous (c).

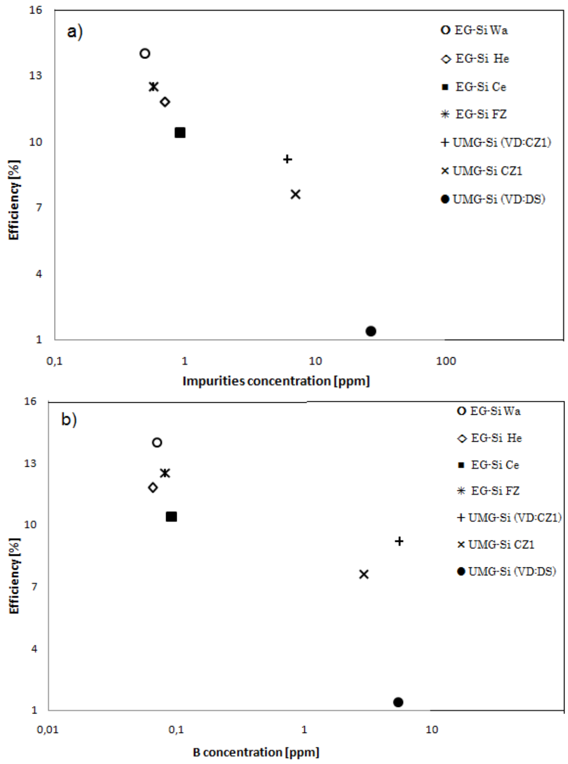

Figure 4: (a) Efficiency of the solar cells as a function of the total concentration of impurities and (b) as a function of the boron concentration.

CONCLUSION

This work describes the use of alternative routes for the purification of metallurgical grade silicon for the manufacture of solar cells. The employment of a combination of vacuum degassing and directional solidification was not effective for the reduction of B and P. The vacuum degassing technique was efficient for the reduction of some impurities with high vapor pressure. It was very efficient to reduce phosphorus impurities, which is not usually achieved using CZ. The combination of the vacuum degassing technique and CZ provided sample with the lowest concentration of impurities compared with the others metallurgical routes. An efficiency of 9,7% was obtained with this material. However, the use of more appropriate process of solar cell fabrication may provide efficiency as high as 13-14% with this material, without further improvement of the quality of the silicon wafer.

Acknowledgment

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