USE OF THE CZOCHRALSKI GROWTH TECHNIQUE TO REMOVE DEFECTS OF POLYCRYSTALLINE UPGRADED METALLURGICAL GRADE SILICON

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ABSTRACT: Upgraded metallurgical grade silicon (UMG-Si) was developed using two different metallurgical routes and used in the fabrication of solar cells. For that purpose, metallurgical grade silicon (MG-Si) was purified by the vacuum degassing (VD) technique. However, solar cells made with this polycrystalline material have poor efficiency due to grain boundary defects. Thus, monocrystalline ingots were growth by the Czochralski (CZ) technique to get monocrystalline wafers, free of grain boundaries. The combined VD with CZ growth routes provided UMG-Si with 99.999% purity and conventional p-n silicon solar of 13% efficiency.
Keywords: silicon, Czochralski, metallurgical-grade.

1 INTRUDUCTION

Current commercial photovoltaic (PV) panels are mainly made using solar cells fabricates with electronic grade crystalline silicon (EG-Si), where the silicon feedstock is purified by the Siemens process. In order to reduce cost in the fabrication of the solar cells, the Siemens process has been replaced by simple processes, but able to produce silicon with purity called "solar grade" (SG-Si), in which high efficient solar cells can be processed, without losing much in the efficiency compared to solar cells made with EG-Si [1, 2]. Some of these approaches adopts a modified Siemens process [3,4].

In this work we adopted two metallurgical routes, vacuum degassing (VD) and Czochralski (CZ) growth, to purify MG-Si to a level that makes possible the fabrication of solar cells of reasonable good efficiency. The reduction in the impurities is achieved mainly by the VD technique. However, this process is used to prepare wafers of polycrystalline silicon. Solar cells made with this material are poor due to a combination of low purity and grain defects. Thus, to eliminate the grain defects we adopted the CZ technique to supply monocrystalline ingots. The CZ technique reduces only slightly the concentration of impurities, but eliminates the grain defects, since one can get monocrystalline silicon using this technique. Thus, using these two processes we could fabricate solar cell of 13 % with potential for higher efficiency using better fabrication process.

2 EXPERIMENTAL

Initially 500g of MG-Si was melted in an electron-beam system (EMO-LEW model) to degas high vapour pressure contaminants. In this process, the melted silicon was held in a vacuum chamber for 30 minutes at a base pressure of 10^{-2} Pa. The process was performed several times to supply few kilograms of purified silicon, which was used in a CZ system to fabricate a monocrystalline silicon ingot. The impurity concentration of the silicon feedstock and the UMG-Si were determined by glow discharge mass spectroscopy (GDMS).

Solar cells were fabricated using a conventional p-n silicon junction, where phosphorous (P) was thermally diffused using $POCl_3$ precursor. To improve que quality of the junction, a gettering process was developed, using P diffusion. Aluminium (Al) back surface field was applied at 800°C. Thermally evaporated Ti/Palladium (Pd)/Silver (Ag) was used for the top and bottom contacts. A tin dioxide (SnO_2) antireflective coating of 75nm thick was deposited adopting the spray pyrolysis technique.

3 RESULTS AND DISCUSSION

The main impurities found in the silicon feedstock, determined by GDMS, are displayed in Fig. 1 together with the impurities of the UMG-Si obtained only by the application of the VD technique (MG-Si+VD) and UMG-Si obtained with the combination of VD and CZ growth (MG-Si+VD+CZ). One can observe that the main reduction in the impurity concentration is achieved by using the VD technique, which was effective for P, Ti, Fe, Al and many other impurities not displayed in the figure. This technique is not good to reduce boron (B) since the vapour pressure of boron is lower than the operating pressure of the electron-bean system (10^{-2} Pa). Adopting the VD only we obtained silicon with 99.9986% purity.

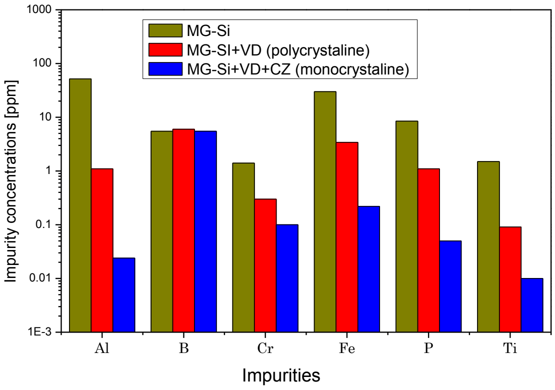

Figure 1: Impurity concentration of the silicon feedstock (MG-Si), UMG-Si obtained by vacuum degassing and UMG-Si obtained by a combination o vacuum degassing and CZ

Using a few kilograms of silicon purified by the VD technique we prepare an ingot using a CZ system. Fig. 1 shows that the impurities concentrations (MG-Si+VD+CZ) also reduce during the CZ process due to segregation phenomena. As can be observed, CZ is not effective in reducing the concentration of B because it has a segregation coefficient close to 1. However, the combination of VD and CZ growth techniques produced material with 99.999% purity.

Using the combination of VD and CZ we obtained monocrystalline silicon with reasonable high purity and free of grain boundary defects. Using these materials we fabricated solar cells in wafers of about 300 micron thick adopting a conventional process as described in the experimental section.

In order to improve the cell efficiency we developed gettering processes based in other experiments using polycrystalline EG-Si reported in literature [5-7]. The idea here was to investigate the differences in the gettering process adopted for poly-EG-Si versus mono-UMG-Si, i.e., high purity/poly versus low purity/mono silicon wafers.

Three different gettering processes (1, 2 and 3) were adopted with the following steps: 1) P diffusion at 900^{o}C, 40 min followed by chemical etch, followed by P diffusion at 900^{o}C, 18 min as the final n^+-layer of the n-p junction; 2) P diffusion at 900^{o}C, 40 min followed by annealing at 900^{o}C, 60 min, followed by chemical etch and the final P diffusion at 900^{o}C, 18 min; 3) P diffusion at 850^{o}C, 50 min, followed by annealing at 850^{o}C, 120 min, chemical etch and final P diffusion at 850^{o}C, 50 min. The final diffusion of each process provided an n^+-layer with sheet resistance of about 20-30 Ohm/square. The solar cells were fabricated using mono-EG-Si and mono-UMG-Si. The basic differences between the three gettering processes were the temperature (850°C or 900°C) and the annealing times.

The effect of the gettering process can be evaluated by comparing the evolution of the diffusion length, Fig. 3. The gettering 1 provided the highest diffusion length for electronic grade silicon (EG-Si), while gettering 3 (850^{o}C) provided the highest value for UMG-Si explaining why those gettering are the best for each material.

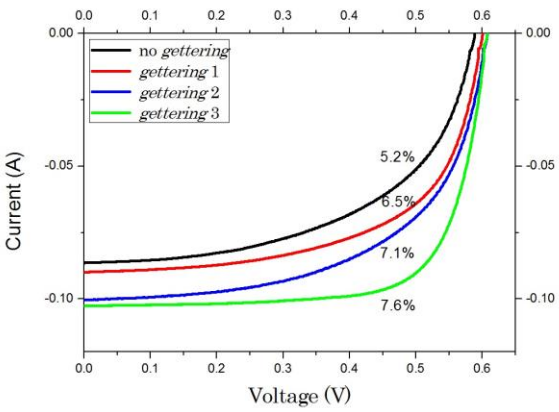

Figure 2: Current vs. voltage curves of the best solar cells fabricated with UMG-Si fabricated with different gettering process

The photovoltaic parameters were obtained by I x V curves, under 100 mW/cm^2 illumination using a solar simulator. Fig. 2 shows the best cell for each of the three gettering process and a the conventional process (without gettering). One can observe that the gettering 1 (900^{o}C) was the best for monocrystalline EG-Si, but for the UMG-Si, the gettering 3 (850^{o}C) provided higher efficiency. At the higher temperature (900°C), some trapped impurities are redistributed within the UMG-Si, which degrades the final efficiency. This effect is partially reduced by adopting the lower temperature of 850°C.

The highest efficiency displayed in Fig. 3 was 7.6 %. However, optimizing the fabrication process we could prepare solar cell on UMG-Si with efficiency as high as 13 %. Using the same processes we got efficiency of 15.5% in monocrystalline EG-Si. It is well know that much higher efficiency can be achieved in EG-Si. Commercial solar cell are fabricated today with efficiency of about 18%. Thus, much higher efficiency is expected for our UMG-Si.

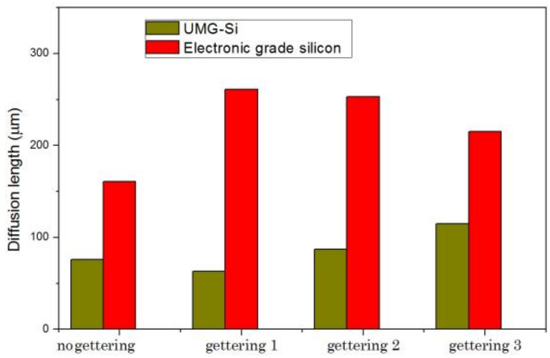

Figure 3: Carrier diffusion length of monocrystalline UMG-Si compared to electronic grade silicon (EG-Si)

Fig. 4 shows the difference in efficiencies of two groups of solar cells, i.e, polycrystalline silicon obtained from the VD process and monocrystalline silicon obtained from the combination of the VD process and CZ.

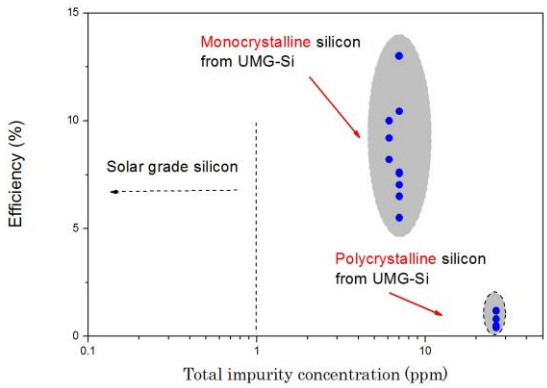

Figure 4: Efficiency vs. total impurity concentration of solar cells made with UMG-Si

The highest efficiency obtained with poly-UMG-Si was about ~1 %, while solar cells of 13% were obtained with mono-UMG-Si. One can notice that the improvement in the material quality is not significant after the CZ growth. The VD wafers (polycrystalline) has about 15ppm impurities, while the VD+CZ (monocrystalline) has about 7 ppm. However, the improvement in efficiency is significant. Thus, the reduction of the impurity concentration obtained by the CZ growth cannot explain the substantial increase in the efficiency. It might be related to the reduction of grain boundary defects that kills the diffusion length of poly-UMG-Si, since the impurity concentration is much higher than the accepted values for solar grade silicon.

4 CONCLUSIONS

We adopted a combination of two techniques to purify metallurgical grade silicon to a level of 99.999% purity and to fabricate solar cell of 13 %, with potential to achieve efficiency higher than 15%. The vacuum degassing technique was effective in reducing the impurity concentration to a reasonable level, while the CZ was efficient in eliminating the grain boundaries defects by supplying a monocrystalline ingot. The difference in efficiency of the solar cells made with materials of about the same concentration of impurity but one been polycrystalline and the other monocrystalline were significant. That improvement justified the extra cost due to the CZ process, since it is also used for the fabrication of commercial silicon wafers using silicon feedstock purified by the Siemen process

ACKNOWLEDGMENT

This work was founded by FAPESP, CNPq, INES/INCT and CAPES. We are also in debt to RIMA Industrial S/A for supplying MG-Si and for performing the CZ growth. We are also grateful for A. A. Coelho for his support in the use of the laboratory CZ system.

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