SOLAR CELLS FROM METALLURGICAL SILICON ZONE MELTED IN POLYCRYSTALLINE SILICON TUBES

G. C. JAIN, S. N. SINGH and R. KISHORE

Division of Materials, National Physical Laboratory, New Delhi 110012 (India)

(Received August 18, 1981; accepted January 11, 1982)

Summary

The results of a new approach to utilize metallurgical grade (MG) silicon powder to obtain polycrystalline silicon wafers for the fabrication of solar cells are reported. A polycrystalline silicon tube is filled with MG silicon powder and is used as a consumable container which facilitates the float zone melting of the powder. This leads to the dilution of impurities in the melt; an *in situ* purification of the melt also takes place during solidification. This method has given an air mass one conversion efficiency of about 4.3% in cells 2 cm^2 in area and there is significant scope for improvement in both the efficiency and the cell area.

1. Introduction

A practical way to reduce the cost of terrestrial solar cells is to utilize low cost metallurgical grade (MG) silicon for the fabrication of solar cells. However, the diffused junction solar cells fabricated from once-pulled MG silicon obtained by the Czochralski (CZ) method have so far exhibited an efficiency η of about 4% or less [1, 2]. To make higher efficiency cells, the deposition of a high purity epitaxial layer onto an MG silicon substrate [3 - 5], twice-pulled CZ MG silicon ingots [2] or zone-refined once-pulled CZ MG silicon ingots has been found to be necessary. In contrast, cells made from refined metallurgical grade (RMG) silicon [6] and solar grade metallurgical (SOMG) silicon [7] have proved to be more efficient. SOMG silicon twice recrystallized by the heat exchanger method (HEM) [8] has yielded diffused junction cells of 12.3% efficiency. However, for low cost solar cells a process consisting of a single recrystallization step, which is capable of providing *in situ* purification of MG silicon during recrystallization, is very attractive. In fact, the HEM [8] is reported to be one such process. It has yielded cells of 7.2% efficiency [8] using MG silicon containing 430 ppm Fe and other impurities with a concentration of less than 54 ppm. In contrast, using MG silicon containing 2000 ppm Fe and other impurities with concen-

trations in the 100 - 800 ppm range, the same process [8] has yielded cells of rather poor efficiency (about 2.1%).

In this paper the results of a new approach for utilizing MG silicon for solar cells are reported. This approach uses the well-known technique of float zone melting which results in an *in situ* purification of the MG silicon during solidification from the melt; it is attractive because of the possibility of removing the dominant impurities, *e.g.* iron, aluminium, copper, titanium, manganese, magnesium, nickel, chromium etc. which, by coincidence, happen to have very low segregation coefficients in silicon (Table 1). In this paper we describe the results of an experiment using this technique.

TABLE 1

Effective segregation coefficient K_{eff} of impurities in silicon and impurity concentrations in SOG silicon, acid-leached MG silicon and in the solidified rod

Impurity	Segregation coefficient K_{eff}[a]	Impurity concentration (at.ppm)		
		SOG Si	Acid-leached MG Si	Solidified Si rod
Fe	6.4×10^{-6}	2 - 6	500	10
Al	2.8×10^{-3}	< 1	1000	10
Cu	8×10^{-4}	0.5 - 1.3	20	1
Ti	2×10^{-6}	< 2	160	< 2
Mn	1.3×10^{-5}	< 1	24	2
Mg	1.3×10^{-6}	5	10	5
Ni	3.2×10^{-5}	0.3 - 2.2	8	4
Cr	1.1×10^{-5}	< 5	< 5	< 5
B	8×10^{-1}	< 10	30	10

[a]K_{eff} = (impurity concentration in solid)/(impurity concentration in liquid).

2. Experimental details

Acid-leached MG silicon powder with a particle size of about 200 μm and with impurities of various concentrations (as given in Table 1) was cleaned by etching it in a mixture of HF, HNO_3 and CH_3COOH solutions (1:5:1 (by volume)) for a short time. A polycrystalline silicon tube which had been etched in an etching mixture of the same composition was then filled with this powder. Mlavsky *et al.* [9] have described the growth of silicon tubes for making tubular silicon solar cells. However, the polycrystalline silicon tube used in this experiment was cast by vacuum suctioning of molten silicon of solar grade (SOG) purity and had internal and external diameters of 7 mm and 10 mm respectively. The concentrations of the various impurities in the SOG silicon are also given in Table 1. The tube was 16 cm long and its bottom end was plugged with a piece of polycrystalline silicon rod 4 cm long and 18 mm in diameter. A 0.5 cm length of this rod

was step ground so that it fitted closely into the polycrystalline silicon tube. The polycrystalline silicon tube was then clamped vertically in a Lepel zone-melting assembly and a molten zone was created at its bottom end in order to join it to the polycrystalline silicon support rod (18 mm in diameter) at the base. The ambient atmosphere consisted of hydrogen with a flow rate of $1.2 \, l \, min^{-1}$. The support rod was rotated at 15 rev min^{-1} and the molten zone was moved up at a rate of 1.8 mm min^{-1}. Simultaneously, the unmelted tube filled with MG silicon was moved down at a rate of 6 mm min^{-1}; this squeezed the liquid zone and increased the diameter of the solidified rod to 18 mm. The process is shown schematically in Fig. 1.

Silicon Tube
o.d — 10mm
i.d.~ 7 mm

Metallurgical Grade
Silicon (Mg-Si) Powder

Quartz Tube

R.F. Load Coil
(Fixed)

Molten Zone

Directionally Frozen
Rod (~18mm dia.)
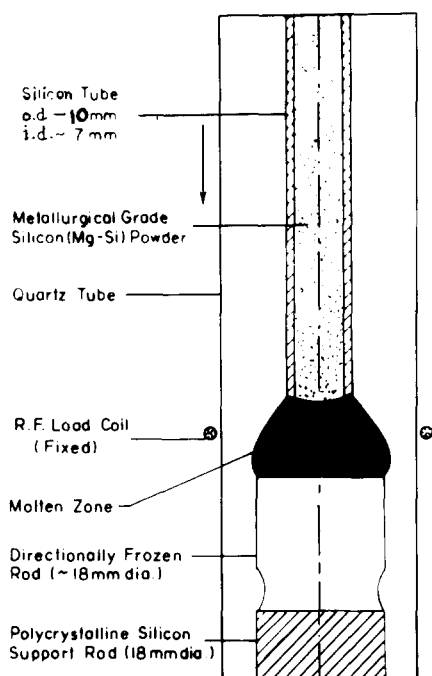
Polycrystalline Silicon
Support Rod (18mm dia.)

Fig. 1. Schematic diagram of the growth of a polycrystalline silicon rod by zone melting MG silicon in a polycrystalline silicon tube.

A rod 3.5 cm long, 18 mm in diameter and of mass 21 g, was grown using 7 g of MG silicon powder and 14 g of SOG silicon, which came from a 15 cm length of the polycrystalline silicon tube. The rod was found to be p type and its resistivity ρ_B varied between 0.22 and 0.39 Ω cm from the starting end to the last part of the frozen end. It was ground to a diameter of 16 mm and was then sliced into wafers 350 μm thick; these were found to be polycrystalline. The concentration of various impurities was measured in a few of these wafers using atomic absorption spectroscopy and spark source emission spectroscopy techniques.

The wafers (initially 350 μm thick) were lapped to a thickness of 280 μm and were chemically polished in a mixture of HF, HNO_3 and

CH_3COOH (1:5:1 (by volume)). The fabrication of n^+–p–p^+ cells was achieved by a simultaneous diffusion of phosphorus from one side of the wafers and of boron from the other side. For this, a thin layer of boro film was spin coated onto one side of each of these wafers and was baked at 200 °C for 20 min in air. Subsequently, the other side was similarly spin coated with a phosphorosilica film and was baked at 110 °C for 30 min. Then the wafers were stacked in a diffusion boat in a back-to-back configuration [10] and were packed compactly. The boat was pushed into a furnace at 1075 °C and the diffusion was carried out for 10 min in a flowing mixture of nitrogen (85 l h^{-1}) and oxygen (15 l h^{-1}) gases. After the controlled removal of the borosilicate glass from over the p^+ region and the phosphosilicate glass from over the n^+ region of the diffused structures in an ice-cooled mixture of HF, HNO_3, CH_3COOH and H_2SO_4 (3:12:5:20 (by volume)) for about 10 s, an edge-etching operation was carried out to eliminate shorting of the junctions at the periphery of these structures [10]. Then, the front and back contacts were made by the vacuum deposition of titanium and silver metal layers and subsequent sintering of these layers at a temperature of 550 °C for 15 min in a hydrogen ambient. The front contact had a double-comb six-finger grid pattern that covered 10% of the cell area, whereas the back contact, which was in the centre, was a full circle 14 mm in diameter. A spin-on titanium silica film was used as an antireflection coating for the n^+ front region. The cell performance was evaluated by measuring the current–voltage (I–V) characteristics at 27 °C under a simulated air mass one (AM1) irradiation of intensity 100 mW cm^{-2}.

3. Results and discussion

The typical grain structure of the wafers is shown in Fig. 2. The grains were columnar along the wafer thickness and the average grain size, as determined by the line intercept method [11], was found to be in the 0.3 - 0.5 mm range. Measurement of the Hall coefficient R_H showed that the net ionized acceptor impurity content of the solidified rod was about 3.0×10^{17} cm^{-3}. From measurements of R_H and ρ_B the Hall mobility at room temperature was determined to be about 95 cm^2 V^{-1} s^{-1}. Table 1 gives the concentrations of various impurities in the MG silicon powder and also in the polycrystalline rod which was grown from it. It was stated in Section 2 that, in all, 14 g of SOG silicon and 7 g of MG silicon were zone melted in order to grow the polycrystalline rod. This implied that a melt composition of 2 parts SOG silicon to 1 part MG silicon was used and hence that, as a result, the impurities were diluted by a factor of 1/3. Thus, the reduction in the boron concentration from 30 at.ppm in MG silicon to 10 at.ppm in the solidified rod may be attributed to the impurity dilution since K_{eff} for boron is close to unity. However, a very much larger decrease in the concentration of aluminium, iron, titanium, copper and manganese showed that there was an *in situ* purification of the MG silicon (by zone refining) during its solidifica-

Fig. 2. Typical grain structure of a polycrystalline silicon slice cut from a zone-refined MG silicon rod (diameter, 16 mm).
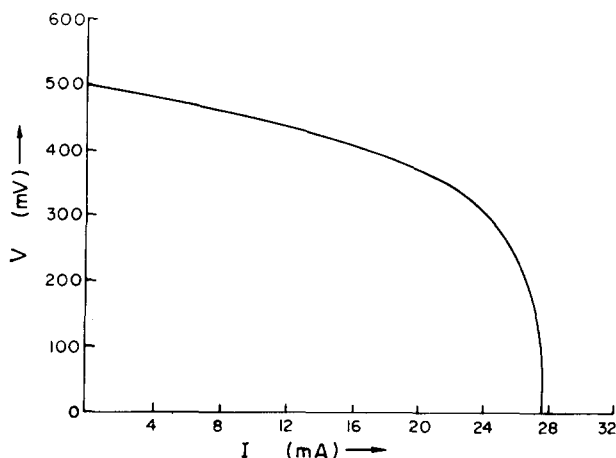
Fig. 3. $I-V$ characteristic of the best cell under a simulated AM1 irradiation of 100 mW cm^{-2} intensity (active cell area, 1.8 cm^2; efficiency, 4.3%).

tion from the molten float zone. This is possible because, unlike boron, these impurities have a K_{eff} which is very much less than unity. Most cells showed $\eta \approx 4\%$ (at AM1); Fig. 3 shows the $I-V$ characteristics of the best cell ($\eta =$ 4.3%). The values of the solar cell parameters, namely the diode ideality factor n, the shunt resistance R_{sh} and the series resistance R_s together with the open-circuit voltage V_{oc}, the short-circuit current I_{sc}, the curve factor CF and the efficiency η, are given in Table 2. R_{sh} and n were determined from the dark reverse $I-V$ characteristic and the $I_{sc}-V_{oc}$ characteristic respectively.

Table 2 shows $\eta = 4.3\%$ which is higher than that reported to have been achieved in cells fabricated by phosphorus diffusion in once-pulled CZ MG

TABLE 2

Measured solar cell parameters at 27 °C[a]

Parameters	Values
V_{oc}	500 mV
I_{sc}	15.3 mA cm^{-2}
η(AM1)	4.3%
R_{sh}	5.5 kΩ
R_s	0.8 Ω
CF	0.557
n	2.78 - 3.0

[a]Active cell area, 1.8 cm^2.

silicon wafers [1 - 3]. The values of I_{sc} achieved in our cells are higher than those reported for once-pulled CZ [2] MG silicon or for RMG silicon and are comparable with those achieved with twice-pulled CZ [2] RMG silicon. A comparison of the diode ideality factor n of our cells with those of the gettered and ungettered cells made from twice-pulled CZ RMG silicon by Saitoh *et al.* [12] would show that our values of n lie between those obtained for the gettered and ungettered cells, 2.1 and 3.9 respectively. A relatively low n in our case compared with the above case of ungettered cells [12] can be attributed to the purification of MG silicon (*i.e.* to the removal of aluminium and other impurities) by zone refining during its solidification from the melt (Table 1). The use of RMG silicon or impurity gettering (*e.g.* by Saitoh *et al.* [12]) can be expected to give higher efficiency cells with this technique. Also, the use of a monocrystalline plug in the bottom end of the rod can be advantageous as it can help to increase the grain size.

4. Conclusions

The zone melting of MG silicon in polycrystalline silicon tubes leads to the dilution of impurities; an *in situ* purification of the MG silicon also occurs during its solidification from the melt. Polycrystalline silicon solar cells with conversion efficiencies of about 4.3% (at AM1) have been fabricated, using this process, in wafers 2 cm^2 in area and there is scope for improvement in both the efficiency and the cell area.

Acknowledgments

References

1 T. L. Chu, S. S. Chu, R. W. Kelm, Jr., and G. W. Wakefield, *J. Electrochem. Soc., 125* (1978) 595.
2 T. Warabisako, T. Saitoh, E. Kuroda, H. Itoh, N. Nakamura and T. Tokuyama, *Proc. 11th Conf. on Solid State Devices, Tokyo, 1979*, in *Jpn. J. Appl. Phys., 19, Suppl. 1* (1980) 539 - 544.
3 T. Saitoh, N. Nakamura, H. Itoh, S. Matsubara, T. Warabisako and T. Tokuyama, *Proc. 13th Photovoltaic Specialists' Conf., Washington, DC, June 5 - 8, 1978*, IEEE, New York, 1978, p. 479.
4 T. L. Chu, *J. Cryst. Growth, 39* (1977) 45.
5 T. L. Chu, S. S. Chu, C. L. Lin and R. Abderrassoul, *J. Appl. Phys., 50* (1979) 919.
6 J. I. Hanoka, H. B. Strock and P. S. Kotval, *Proc. 13th Photovoltaic Specialists' Conf., Washington, DC, June 5 - 8, 1978*, IEEE, New York, 1978, p. 485.
7 C. P. Khattak, F. Schmid and L. P. Hunt, *Novel Silicon Growth Methods Conf., St. Louis, Princeton, 1980.*
8 F. Schmid, M. Basaran and C. P. Khattak, *Proc. 3rd Commission of European Communities Conf. on Photovoltaic Solar Energy, Cannes, October 27 - 31, 1980,* Reidel, Dordrecht, 1981, p. 252.
9 A. I. Mlavsky, H. B. Serrege, R. W. Stormont and A. S. Taylor, *Proc. 12th Photovoltaic Specialists' Conf., Baton Rouge, LA, November 15 - 18, 1976*, IEEE, New York, 1976, p. 160.
10 G. C. Jain, S. N. Singh, R. K. Kotnala and N. K. Arora, *J. Appl. Phys., 52* (1981) 4821.
11 C. S. Smith and L. Guttman, *Trans. AIME, 197* (1953) 81.
12 T. Saitoh, T. Warabisako, E. Kuroda, H. Itoh, S. Matsubara and T. Tokuyama, *IEEE Trans. Electron Devices, 27* (1980) 671.