SAND94-1588C
Conf-941203--18

HIGH-EFFICIENCY SOLAR CELLS USING HEM SILICON

C. P. Khattak¹, F. Schmid¹, and W. K. Schubert²¹Crystal Systems, Inc., 27 Congress Street, Salem, MA 01970-5597, USA²Sandia National Laboratories, Albuquerque, NM 87185-0752, USA

ABSTRACT

Developments in Heat Exchanger Method (HEM) technology for production of multicrystalline silicon ingot production have led to growth of larger ingots (55 cm square cross section) with lower costs and reliability in production. A single reusable crucible has been used to produce 16 multicrystalline 33 cm square cross section 40 kg ingots, and capability to produce 44 cm ingots has been demonstrated. Large area solar cells of 16.3% (42 cm²) and 15.3% (100 cm²) efficiency have been produced without optimization of the material production and the solar cell processing.

As mentioned above, silica crucible cost reductions may be limited by the cost of the raw materials. Furthermore, devitrification of the fused silica during ingot production prevents reuse of the crucibles. Therefore, another avenue for cost savings is the use of reusable crucibles made from other crucible materials. It is essential, in this approach, to retain purity of the silicon ingot so that solar cell efficiencies are not compromised. The feasibility of reusing crucibles was established [7] previously by producing multicrystalline silicon ingots in the same crucible with the HEM process. This paper also reports progress with reusable crucibles and documents the quality of the material produced through the high performance of solar cells made from it.

INTRODUCTION

Multicrystalline silicon ingot technologies [1-6] offer promise for cost-effective, high-efficiency material for photovoltaic applications. These approaches are becoming the mainstay for current production of modules for power generation. This paper reports the progress made in the Heat Exchanger Method (HEM) technology to increase ingot size and throughput from furnaces, improving efficiencies of solar cells, and adopting the use of reusable crucibles to achieve further cost reductions.

All processing component costs for ingot technology have been reduced. On the basis of these costs, the proportion of expendable materials costs is high and therefore getting renewed interest. Reduction of crucible costs is key to achieving economic silicon ingot production. Most ingot technologies use silica crucibles because silica is available in high purity form at relatively low cost. Raw material costs limit the potential for further reductions in the cost of the silica crucible itself. The crucible contribution to the total ingot cost could be reduced further by increasing the ingot size. In addition, throughput can be increased with larger ingots and energy costs reduced if the processing time can be held constant. Material quality is expected to improve with larger ingot size due to reduced surface to volume ratio for large size. This translates to reduced cost per watt for the solar cells produced from the ingot.

HEM SILICON FROM SILICA CRUCIBLES

The HEM has been used for production [8] of 44 cm square cross section silicon ingots using high purity fused silica crucibles which were heat treated prior to use to promote crucible delamination and prevent cracking of the solidified silicon ingot. It was necessary to use silica crucibles with graphite plates because the ingot solidification temperature was above the softening point of fused silica. Ingots grown in silica crucibles showed distortion and taper, and oversize ingots had to be produced to yield bars to specification.

Growth of silicon ingots was carried out by HEM under vacuum. Modifications were made to the HEM furnace and the heat exchanger system so the crucible could be lowered in the heat zone. This improved reliability in reproducible growth of the 80 kg charge and the feasibility of producing 100 kg ingots [1].

As mentioned above, the heat-treated silica crucible relied on the devitrification of the fused silica interior during growth, causing delamination of the crucible during cool-down and preventing ingot cracking. It was necessary to develop a HEM cycle which was compatible with growth of silicon and for devitrification of the fused silica crucible. The reliability of the heat-treated fused silica crucible decreased as the size of the ingot was increased.

In order to decouple the ingot growth and the crucible delamination parameters, a coated silica crucible was developed for HEM silicon ingot production. Various silicon-nitride-based coatings were applied to the inside surfaces of a slip-cast fused silica crucible. The coating

² This author's contribution was supported by the Photovoltaic Technology Division, U.S. Department of Energy, Contract DE-AC04-84AL85000.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

JR

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

**Portions of this document may be illegible
electronic image products. Images are
produced from the best available original
document.**

was meant to prevent attachment of the silicon ingot to the crucible during growth, and to prevent impurities from the crucible from contaminating the silicon ingot. The silicon-nitride-based coatings were not stable at the growth temperatures under vacuum; the HEM processing was, therefore, carried out under inert gas atmosphere to avoid decomposition of the coating.

Multicrystalline silicon ingots weighing 90 kg with 44 cm square cross-section were grown using this approach. This ingot was geometrically square with flat sides, and controlled growth was achieved in the corners. Characterization showed that all the characteristics of HEM silicon produced in heat treated silica crucibles were retained and that the production of high performance solar cells was not compromised. A mapping of the resistivity of a slab sectioned parallel to one of the square sides shows that extremely good uniformity of electrical properties was achieved (see Fig. 1).

Fig. 1. Cross section of a 44 cm ingot and mapping of resistivity (in ohm-cm) showing uniformity in structure and electrical properties.

The reliability of the coated crucible, and decoupling of the HEM processing cycle for ingot solidification and crucible delamination, allowed increase in the size of the ingots. Figure 2 shows a 55 cm square cross section multicrystalline silicon ingot grown by HEM in a silica crucible. All the desirable characteristics of controlled growth were retained as the ingot size was increased. Controlled growth is confirmed because the last material to solidify is very close to the corners; this material is identified by the tip of silicon in the four corners due to expansion of the last silicon solidified.

HEM SILICON FROM REUSABLE CRUCIBLES

The essential requirements of a reusable crucible for directional growth of multicrystalline silicon ingots are:

- compatibility with silicon ingot growth to prevent ingot or crucible cracking,
- a crucible material which is stable at the processing temperature for directional growth,
- feasibility to coat to prevent attachment of silicon,
- non-contamination of the silicon which reduces solar cell performance,
- a softening temperature higher than the growth temperature,
- fabrication in large sizes and desired square shapes achievable at low cost, and
- crucible reusable multiple times to reduce cost.

Based upon these requirements, a high temperature non-oxide ceramic crucible was selected and reported on [7]. Such a crucible was used to produce several 40 kg, 33 cm square cross-section ingots without degradation of the silicon or the crucible. Characterization of the silicon showed vertically oriented grain boundaries, uniformity in resistivity, low dislocation density, diffusion lengths up to 270 μm , and less than 1 ppm oxygen concentration. Solar cells of 2 cm x 2 cm size showed efficiencies over 15% [7].

The reusable crucibles were manufactured with a square cross section and a slight taper to the side walls to aid removal of the ingot after growth. A silicon-nitride-based coating was applied to the inside surfaces of these crucibles. Ingot growth was carried out by HEM using processing parameters similar to those developed for a coated silica crucible. The developmental effort was carried out at 40 kg, 33 cm square cross-section ingot size, and a single crucible was used to produce 16 ingots. Characterization of the ingots showed the performance of the material remained consistent with the number of times the crucible was used.

In addition to reduced crucible costs for the production of multicrystalline silicon ingots, the material utilization was also improved. This was achieved because the high temperature ceramic crucible material did not show distortion after ingot growth; therefore, ingots could be produced closer to finished size to improve ingot utilization. These ingots were of reproducible size, and only the tapered side walls and the bottom and top surfaces of the

Fig. 2. A 55 cm square cross section multicrystalline silicon ingot grown by HEM showing controlled growth.

Ingots had to be removed; the rest of the material could be sliced for solar cells.

Multicrystalline silicon grown in reusable crucibles showed less than 1 ppm oxygen concentration [9]. This concentration is much lower than silicon solidified in silica crucibles [10]. Oxygen contamination is due to reaction of molten silicon with the silica crucible [11]; a non-oxide, ceramic crucible, therefore, does not cause contamination of silicon from oxygen.

Once the reliability of the reusable crucibles was demonstrated, the crucible size was increased to 44 cm square cross-section. Silicon ingots weighing 65 kg were directionally grown by HEM. The height of these ingots was less than produced in silica crucibles because the reusable crucibles were shorter. Characterization of multicrystalline silicon ingots produced in reusable crucibles showed that the quality of silicon was not compromised and was of performance similar to silicon produced in silica crucibles.

SOLAR CELL PERFORMANCE

Several ingots produced in fused silica and reusable crucibles were sectioned to approximately 10 cm x 10 cm cross section bars. Large size grains (1-2 cm) with vertically oriented grain boundaries were produced. Resistivity of the silicon was consistent with doping and segregation effects.

Wafers were processed to characterize both lateral uniformity and uniformity along the growth direction. An array of 2 cm x 2 cm cells was produced on 10 cm x 10 cm wafers taken from the top, middle and bottom of ingots. Average wafer efficiencies (8 cells/slice) of 15.8% were achieved during initial characterization of the material on wafers taken from the middle of an ingot.

The best efficiency of individual cells produced in either a reusable or a coated silica crucible, using the same processing techniques, is shown in Table I. While the solar cell efficiencies are the same, slight differences in performance parameters can be explained by differences in resistivity and lower oxygen concentration for silicon grown in a reusable crucible. This data shows that the quality of silicon grown by HEM using the two types of crucibles is quite similar.

Table I. Performance of Solar Cells (2 cm x 2 cm) during initial evaluation of HEM silicon produced using different crucibles.

Crucible	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	Eff. (%)
Silica	0.616	34.00	79.2	16.6
Reusable	0.623	33.23	80.1	16.8

Data for variation in solar cell performance as a function of position in the ingot showed that the highest efficiency for HEM silicon corresponds to the middle section of the bar with a slight deterioration in performance near the top of the ingot and bottom of the ingot. Slight deterioration at the bottom of the ingot may be due to thermal stress because this material undergoes maximum thermal gradient during ingot growth. The degradation in performance near the top of the ingot may be due to segregation of impurities during growth.

HEM silicon was processed into high performance solar cells at the University Center of Excellence for Photovoltaics and Education, Georgia Institute of Technology, and solar cells of 17.4% efficiency were produced (1 cm²) using this approach [12]. The characteristics of this solar cell were confirmed at National Renewable Energy Laboratory (NREL).

LARGE AREA SOLAR CELL FABRICATION

Based upon characterization data of HEM silicon, Sandia National Laboratories produced high performance modules with this material. The target for the module was module efficiency in excess of 15% using solar cells of 42 cm² area. The first batch of 12 cells (41.98 cm² area) yielded an average efficiency of 16.0 ± 0.2% with a range of values between 15.6 and 16.3% (Table II). For this effort 72 cells were fabricated, and 68 were completed; three of these cells broke during processing, and one broke during testing. The cells ranged in efficiency from 15.0 to 16.3% with an average value of 15.6% [13]. Two modules were fabricated, and the module efficiencies were over 15% under standard test conditions [14].

Table II. Characteristics of one batch of 42 cm² solar cells produced using HEM multicrystalline silicon.

Wafer	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	Eff (%)
1	0.608	33.83	79.2	16.3
2	0.609	33.80	79.2	16.3
3	0.608	33.66	78.8	16.1
4	0.607	34.14	77.6	16.1
5	0.608	33.90	79.0	16.3
6	0.605	33.40	78.1	15.8
8	0.609	33.83	78.5	16.2
9	0.605	33.47	77.9	15.8
10	0.603	33.11	78.0	15.6
11	0.605	33.30	79.1	15.9
12	0.609	33.73	78.3	16.1
13	0.603	33.40	78.7	15.9
Mean	0.607	33.63	78.5	16.0
s.d.	0.002	0.29	0.5	0.2

During a recent experiment at ASE Americas, a number of different solar grade based materials were processed through the high throughput production line to compare

performance with that of EFG material. This production line was optimized for EFG material and combines a number of process steps to improve substrate quality. It incorporates high throughput production features; upgrading is entirely in the process and does not affect its throughput or costs.

The diffusion and phosphorous gettering occurs in a high throughput belt furnace process [15]. Antireflection coating is combined with passivation [16]. A full area aluminum back contact is used and regrown at 850° C to provide both gettering and a back surface field [17, 18] and a front silver metallization is applied that is fired through a silicon nitride coat to complete the process [19, 20]. All these steps are integrated in a line with a throughput of approximately 700 cells/hour (10 cm x 10 cm). The data of a batch of 21 cells processed from HEM silicon is shown in Table III (cell measurements were done at ASE Americas). These results were achieved without optimization of HEM silicon processing or tailoring the cell process to the material. This data (Table III) shows an average cell efficiency of 14.13% with a maximum value of 15.3%.

Table III. Performance of 100 cm² solar cells produced by ASE Americas using HEM multicrystalline silicon.

Cell	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	Eff (%)
1	0.6019	30.29	72.88	13.29
2	0.5944	28.84	73.38	12.57
3	0.6094	31.11	74.99	14.22
4	0.5937	29.15	73.97	12.88
5	0.6156	32.31	74.90	14.90
6	0.5983	28.81	73.03	12.55
7	0.6160	32.12	75.89	15.02
8	0.6129	31.75	74.50	14.50
9	0.6136	31.81	74.58	14.58
10	0.6035	30.10	75.49	13.71
11	0.6158	32.33	76.09	15.15
12	0.6158	32.22	77.09	15.29
13	0.6143	32.08	76.35	15.05
14	0.6102	31.48	72.97	14.02
15	0.5992	29.79	73.41	13.10
16	0.6119	31.71	75.73	14.70
17	0.6140	32.22	72.88	14.42
18	0.6130	31.52	74.78	14.45
19	0.6160	32.27	75.36	14.98
20	0.5991	29.46	74.01	13.06
21	0.6102	31.12	75.30	14.30
Mean	0.608	31.07	74.64	14.13
s.d.	0.008	1.24	1.24	0.89

CONCLUSIONS

Two independent approaches have been developed to reduce the crucible cost contribution for multicrystalline silicon ingot production by HEM. A coated silica crucible has been used for improved cross-section, 90kg silicon ingots. Growth of silicon ingots in reusable crucibles has also been extended to 44 cm square cross-section size and 16 ingots have been produced using one crucible.

Solar cells fabricated from multicrystalline silicon produced in silica or reusable crucibles have shown high performance with minor variations. Efficiencies of 17.4% (1 cm²), 16.3% (42 cm²) and 15.3% (100 cm²) have been demonstrated. Over 15% efficiency modules have been fabricated using HEM multicrystalline silicon.

Larger ingot growth and high performance of HEM silicon will allow major cost reduction of solar cell production. Controlled growth of 55 cm square ingots will achieve economies near term and the impact of reusable crucibles will be beneficial for the future.

REFERENCES

- [1] G. P. Khattak, F. Schmid, D. W. Cunningham and J. G. Summers, "Directional Solidification of 80 kg Multicrystalline Silicon Ingots by HEM", *Twenty-Second IEEE PVSC*, 1991, pp.976-978.
- [2] D. Helmreich, "The Wacker Ingot Casting Process" in: *Silicon Processing for Photovoltaics II*, eds. C. P. Khattak and K. V. Ravi (North Holland, Amsterdam, 1987) pp.97-151.
- [3] W. F. Regnault and K. C. Yoo, "Lifetime Enhancement in Semicrystalline Silicon by Structural Defect Density Reduction", *Seventeenth IEEE PVSC*, 1984, pp.286-291.
- [4] J. Fally and C. Guenel, "Study of the Elaboration of Semicrystalline Silicon Ingots", *Third E. C. PSEC*, 1980, pp.598-602.
- [5] I. A. Dorrity, B. J. Garrard and D. A. Hukin, "Polycrystalline Photovoltaic Silicon Ingot Production", *Tenth E. C. PSEC*, 1991, pp.317-319.
- [6] W. Koch, W. Krumba, H. Lange, W. Schmidt, F. Schomann and G. Wahl, "Development of Cost Effective Silicon Material- and Cell-Fabrication-Processes for High Efficient Large Area Terrestrial Solar Cells", *Twelfth E. C. PSEC*, 1994, pp.797-798.
- [7] G. P. Khattak, F. Schmid, W. K. Schubert, M. Cudzinovic and B. L. Sopori, "Characteristics of HEM Silicon Produced in a Reusable Crucible", *Twenty-third IEEE PVSC*, 1993, pp. 73-77.
- [8] C. P. Khattak and F. Schmid, "HEM Technology for Photovoltaic Applications", *PVSEC-5*, pp.117-124.

[9] C. P. Khattak, F. Schmid, M. Cudzinovic and B. L. Sopori, "Impurity/Defect Analysis of HEM Silicon", *Third Workshop on the Role of Point Defects and Defect Complexes in Silicon Device Processing*, 1993, pp.13-18.

[10] K. A. Dumas, C. P. Khattak and F. Schmid, "Characteristics of HEM Silicon for Solar Cells", *Fifteenth IEEE PVSC*, 1981, pp.954-958.

[11] F. Schmid, C. P. Khattak, T. G. Digges, Jr. and L. Kaufman, "Origin of SiC Impurities in Silicon Crystals Grown from the Melt in Vacuum", *J. Electrochem. Soc.* 126, 1979, pp.935-938.

[12] A. Rohatgi, Georgia Institute of Technology, personal communication.

[13] W. K. Schubert, D. S. Ruby, P.A. Basore, J. M. Geø, M. E. Buck, and H. L. Tardy, "A Simple Single Photomask Process for Fabrication of High-Efficiency Multicrystalline Silicon Solar Cells", *This conference*.

[14] D. L. King, W. K. Schubert and T. D. Hund, "World's First 15%-Efficient Multicrystalline Silicon Modules", *This Conference*.

[15] M. D. Rosenblum and J. I. Hanoka, *U. S. Patent* 5,270,248.

[16] A. R. Chaudhuri and K. V. Ravi, *U. K. Patent* GB 2215 129 B.

[17] F. J. Bottari, J. I. Hanoka, and F. W. Sylva, *U. S. Patent* 5,151,386.

[18] J. A. Amick, F. J. Bottari and J. I. Hanoka, *J. Electrochem. Soc.* (to be published).

[19] J. I. Hanoka and S. E. Danielson, *U. S. Patent* 5,151,377.

[20] J. I. Hanoka, *Canadian Patent* 1,323,452.