J Mater Sci (2011) 46:1044–1048
DOI 10.1007/s10853-010-4870-0

The materials characteristic and the efficiency degradation of solar cells from solar grade silicon from a metallurgical process route

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Received: 29 March 2010 / Accepted: 23 August 2010 / Published online: 8 September 2010

Abstract The rising conventional energy prices have opened up the market for photovoltaic, but the lack of polycrystalline silicon from the chemical route restricts the growth of crystalline silicon solar cells. Recently there is a trend that produces solar cells by using the newly developed solar grade silicon feedstock from a metallurgical process route. In this article, the chemical components of solar grade silicon feedstock are analyzed. The single crystalline silicon solar cells from 100% solar grade silicon feedstock from a metallurgical process route are investigated. The outdoor performance of solar modules encapsulated by such cells is reported. The experimental evidence suggests that such solar cells can achieve the average efficiency higher than 14% on single crystalline silicon wafers. However, the efficiency degradation of solar cells under natural sunlight is significant, and the electrical uniformity of small cells diced from the whole cell is too bad. The metal impurities, oxygen, carbon, and their complexes influence the performance stabilization. The article proves that the module made by such cells has a big cell mismatch loss than normal cells made by electronic grade silicon, even if these cells come from the same sort. And the operating temperature of the cells of the modules is 15–22 °C higher than normal modules under the same conditions. The solar grade silicon feedstock from a metallurgical process route has to be improved farther in order to be used in photovoltaic industry.

Introduction

Because of feed-in-tariff for photovoltaic, the world photovoltaic market is booming with over 50% per annum growth in recent years [1]. People do not doubt that the photovoltaic is the solution for our future energy. The impressive growth is mainly based on solar cells made from polycrystalline silicon. Thus the lack of polycrystalline silicon from the chemical route restricts the growth of crystalline silicon solar cells. Therefore people try to produce solar cells by using the newly developed solar grade silicon feedstock from a metallurgical process route [2, 3]. This route for production can be five times more energy efficient than the conventional Siemens process that uses more than 200 kWh/kg [4]. Some authors reported that they had achieved efficiencies higher than 16% on multicrystalline wafers containing a significant amount of the solar grade silicon feedstock from a metallurgical process route, but they did not show the efficiency degradation and reverse current of these solar cells, and also did not show the outdoor performance of solar modules encapsulated by the single crystalline silicon solar cells from 100% solar grade silicon feedstock from a metallurgical process route [5, 6]. At present, some silicon wafers factories make a cylindrical ingot by solar grade silicon feedstock from a metallurgical process route, which is blended with electronic grade silicon. These solar cells have also a remarkable degradation when placed under the natural sunlight. Although many research works have been performed, the origins of the degradation are still not understood from atomistic viewpoints. The charge states and the lattice positions of iron impurities are not well-known for the

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isolated states as well as the associated states with the lattice defects at the process temperatures and also during the operation under sunlight [7].

In this article, the chemical components of solar grade silicon feedstock are analyzed; the single crystalline silicon solar cells from 100% solar grade silicon feedstock from a metallurgical process route are investigated. The outdoor performance of solar modules encapsulated by such cells is reported. The experimental evidence suggests that such solar cells can achieve the average efficiency higher than 14% on single crystalline wafers. However, the efficiency degradation of solar cells under natural sunlight is significant, and the electrical uniformity of small cells diced from the whole cell is too bad. The metal impurities, oxygen, carbon, and their complexes influence the performance stabilization. The paper also proves that the module made by such cells has a big cell mismatch loss than normal cells, even if these cells come from the same efficiency. The operating temperature of the cells of the modules is 15–22 °C higher than normal modules under the same conditions. The solar grade silicon feedstock from a metallurgical process route has to be improved farther in order to be used in photovoltaic industry.

Experimental methods

Solar grade silicon from a metallurgical process route was produced by Nan'an Sanjing Silicon Refining Co., Ltd., in China. The commercial metallurgical grade silicon was treated with hydro-metallurgical refining process including slag treatment, alloying, and leaching. After the first Czochralski process had finished, the cylindrical ingot was crushed, and 99.9995% purity silicon was obtained. A p-type boron doped cylindrical ingot of single crystal silicon was grown by the second Czochralski process. Slicing of 220 μm thickness wafers from a cylindrical ingot used a conventional wire saw technique. The wafers have an area of 125 × 125 mm^2 with about 1 Ω cm resistivity. Lifetime measurements had been carried out on one of these wafers to assess the electronic quality of this material by WT-2000.

The solar cell processing used is based on industrialized process steps, as the same as those made from polycrystalline silicon from the chemical route.

After lifetime measurements, the as-cut wafers were treated by chemical iso-texture for saw damage etch and light trapping, the texturisation process was done in two steps, the first step was to remove damage on the surface caused by sawing. This step was carried out in about 20% NaOH solution kept at 80 ± 2 °C. This removed about 30 μm outer layer from all sides, the second step was to produce straight upright pyramids on a freshly prepared surface. After a thorough wash in flowing deionized water, the wafers were etched in a solution consisting of 1.0% NaOH and 20% isopropyl alcohol by volume at 80 ± 2 °C. The wafers were washed in the flowing deionized water followed by boiling in dilute HCl to remove the metallic impurities. Finally, the wafers were washed again in the flowing deionized water and were dried with an air jet.

The wafers were then diffused using liquid $POCl_3$ as the dopant source to form an emitter with a sheet resistivity of 40–45 Ω/square. The junction depth was about 0.4 μm. After $POCl_3$ diffusion, edge isolation was performed by plasma etching.

The SiNx:H thin films were prepared by plasma enhanced chemical vapor deposition (PECVD) using SiH_4 and NH_3. The imaginary part (extinction coefficient) of these films was nearly zero in the measured wavelength region of 0.3–0.8 μm; the refractive index is 2.0 at a wavelength of 632.8 nm [8].

The metallization was carried out in a conventional way, silver and aluminum pastes were screen printed to top and back surface of wafers, which then formed electric contact of solar cells through a rapid thermal processing at about 760 °C for 3–5 s. The testing and sorting of solar cells were performed by Berger testing system, in order to improve the output power of the entire module.

The tabbing and stringing of solar cells were carried out by manual welding. After string bussing, the module was encapsulated in the following way: glass/EVA/cell/EVA/tedlar/polyster/tedlar, where EVA stands for ethyl vinyl acetate. The module performance testing was carried out by Spire 460.

Then the outdoor exposure experiments were conducted. Figure 1 shows the scene of the outdoor experiments. The sunlight exposure dose was measured by YFJ-10 solar irradiation meter; the operation temperature of module was measured by thermocouple. When measured every time, the solar simulator was calibrated by the standard module.

The typical process sequence used in the experiments is shown in Table 1.

Fig. 1 The scene of the outdoor sunlight exposure

Table 1 Process sequence from metallurgical grade silicon to solar module

Step no.	Process description
1	Metallurgical grade silicon
2	Refining
3	Solar grade silicon
4	CZ–Si growth
5	Slicing
6	Saw damage removal and surface texturing
7	Edge isolation by plasma etching
8	SiNx:H deposition
9	Screen-printing of Ag rear side, Al rear side, and Ag front side
10	Firing through
11	Testing and sorting
12	Tabbing and stringing
13	Bussing and lay-up
14	Lamination
15	Trimming and framing
16	I–V testing

Results and discussion

Chemical analysis of solar grade silicon

The impurities of solar grade silicon wafer from a metallurgical process route were determined by ICP-MASS made by Kwicklink. The impurities and contents are shown in Table 2. Not surprisingly, some metal impurities may be present in a number of different chemical forms, such as point-like (interstitial or substitutional), or in precipitates in these silicon materials. These unwanted metallic impurities are the cause of a large fraction of the total recombination events in solar cells made from a metallurgical process route. It plays a significant role in reducing the efficiency of crystalline silicon solar cells, and causing a large light-induced degradation [7].

From Table 2, we find that Fe, Cr, Cd, and Hg are the most abundant and Mn, Co, Mo, Ag, Ni, Ti, Au, and V are at low concentrations.

Most transition metals occur as interstitial impurities when present in silicon. Ni, Cu, and Co are rapid diffusers, and have some effect on crystalline silicon solar cells.

Fe, Cr, and Mn remain very slightly mobile even at room temperature, giving rise to their well-known property of forming pairs with positively-charged ionized dopant atoms such as B, Ga, and Al [9]. Fe carries a positive charge when ionized in single crystalline silicon; it is more attractive as traps to electrons, so it leads to greater recombination activity in P-type silicon than in N-type silicon. Nevertheless, in the process of fabricating solar cells, we may minish its effect on solar cells by double-faced diffusion.

From Table 2, we find that the concentration of impurities for solar grade silicon wafer from a metallurgical process route are higher than the polycrystalline silicon

Table 2 The results of chemical analysis for solar grade silicon wafer from a metallurgical process route

Element	Concentration (ppm wt)	Element	Concentration (ppm wt)	Element	Concentration (ppm wt)	Element	Concentration (ppm wt)
Li	<0.01	Ag	<0.01	Co	<0.01	Er	<0.005
Be	<0.005	Cd	<0.1	Ni	<0.01	Tm	<0.005
B	<2	In	<0.01	Cu	<0.05	Yb	<0.005
F	<1	Sn	<0.06	Zn	<0.05	Lu	<0.005
Na	<0.01	Sb	<0.05	Ga	<0.05	Hf	<0.01
Mg	<0.05	Te	<0.06	Ge	<0.05	Ta	<100
Al	1.3	I	<0.01	As	<0.05	W	<0.01
Si	Matric	Cs	<0.005	Se	<0.06	Re	<0.01
P	<10	Ba	<0.005	Br	<0.05	Os	<0.01
S	<0.06	La	<0.005	Rb	<0.05	Ir	<0.01
Cl	<0.05	Ce	<0.005	Sr	<0.01	Pt	<0.01
K	<0.05	Pr	<0.005	Y	<0.01	Au	<0.05
Ca	<0.05	Nd	<0.005	Zr	<0.01	Hg	<0.1
Sc	<0.05	Sm	<0.005	Nb	<0.01	Ti	<0.01
Ti	<0.01	Eu	<0.005	Mo	<0.05	Pb	<0.05
V	<0.005	Gd	<0.005	Ru	<0.01	Bi	<0.01
Cr	<0.1	Tb	<0.005	Rh	<0.005	Th	<0.005
Mn	<0.01	Dv	<0.005	Pd	<0.01	U	<0.005
Fe	0.29	Ho	<0.005				

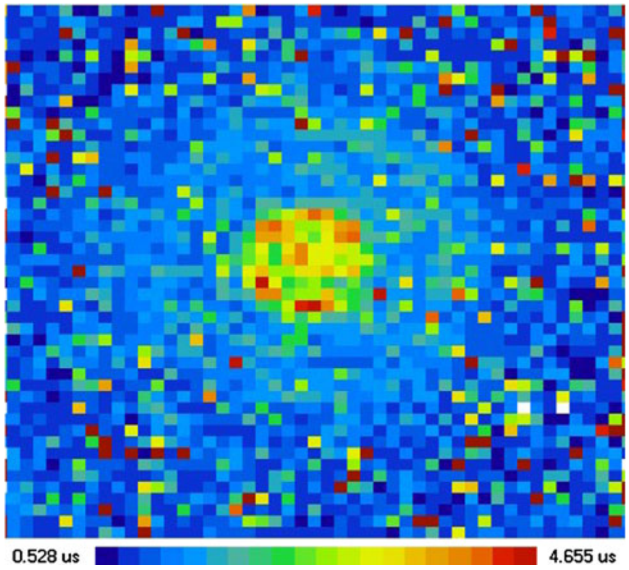

Fig. 2 Bulk lifetime mapping of a 125 × 125 mm^2 silicon wafer from 100% solar grade silicon feedstock from a metallurgical process route

from the chemical route, these impurities affected the efficiency and degradation of solar cells. Before the mass production of the single crystalline silicon solar cells from solar grade silicon feedstock from a metallurgical process route. This puzzle must be solved by defect engineering, in which appropriate treatments could be developed to coax the impurities into their most benign distribution and chemical state [7].

Lifetime measurements of solar grade silicon wafers

Figure 2 shows minority carrier lifetime for one of the wafers from 100% solar grade silicon feedstock from a metallurgical process route. The average lifetime of this wafer is 1.135 μs, but the distribution of lifetime is not uniform. The same problems could be found in some solar grade silicon wafer from a metallurgical process route manufactured by other factories. This is probably common in solar grade silicon wafer from a metallurgical process route.

The performance of solar grade silicon solar cells and electrical uniformity over a whole cell

After testing and sorting, the performance of partial solar grade mono-crystalline silicon solar cells from a metallurgical process route are listed in Table 3. Where Pm is maximum power point power, Um is maximum power point voltage, Im is maximum power point current, Uoc is open circuit voltage, Isc is short circuit current, FF is fill factor, Ncell is efficiency, and Irev1 is reverse current at −12 V.

Table 3 The results of solar cells made from 100% solar grade silicon wafers from a metallurgical process route measured under standard testing conditions (25 °C, 1000 W/m^2, AM1.5)

Pm	Um	Im	Uoc	Isc	FF	NCell	Irev1
2.112	0.482	4.382	0.597	4.722	74.924	0.142	4.147
2.146	0.493	4.353	0.605	5.116	69.335	0.144	3.293
2.164	0.474	4.565	0.619	5.155	67.811	0.146	5.209
2.175	0.490	4.439	0.622	5.151	67.889	0.146	3.173
2.186	0.472	4.631	0.626	5.296	65.932	0.147	4.244
2.189	0.486	4.504	0.596	4.880	75.261	0.147	4.216
2.199	0.482	4.562	0.597	4.883	75.430	0.148	4.263
2.200	0.486	4.526	0.598	4.904	75.007	0.148	3.266
2.206	0.495	4.457	0.605	5.135	71.015	0.149	3.263
2.206	0.488	4.521	0.625	5.105	69.148	0.149	2.093
2.211	0.496	4.458	0.601	4.888	75.269	0.149	3.263
2.221	0.486	4.569	0.602	4.889	75.447	0.149	3.257

The size of the cells is 125 × 125 mm^2

From Table 3, we find that the reverse current of solar grade mono-crystalline silicon solar cells from a metallurgical process route is bigger than normal solar cells. When the above solar cell (125 × 125 mm^2) is cut into four pieces along the cross with a laser, we find that the distribution of electrical performance is fairly non-uniform. It may be caused by abundant carbon and nitrogen in such silicon materials. SiC and SiN creates conductive pathways that can potentially produce shunts across the p–n junction of a solar cell [7].

Performance of modules and outdoor experiments

The above 72 cells were encapsulated into a module in a 6 × 12 matrix connected in series. After lamination, the modules were measured under standard testing conditions (25 °C, 1000 W/m^2, AM1.5). The electrical parameters of the experimental modules are indicated in Table 4.

By comparison, we find that the module made by such cells has a big cell mismatch loss than normal cells, even if these cells come from the same efficiency. Then, two of the modules were stressed with real-time outdoor exposure. Figure 3 shows the result of light-induced degradation. After a 15.7 kW$_p$h/m^{2}of accumulated solar irradiation, the rate of degradation of Module 1 is −30.8%, the rate of

Table 4 The electrical parameters of experimental modules

Pm(W)	Im(A)	Vm(V)	Isc(A)	Voc(V)
149.01	4.24	35.18	4.65	42.18
149.99	4.29	34.94	4.60	42.73
147.72	4.18	35.38	4.58	43.07
148.18	4.25	34.89	4.55	42.87

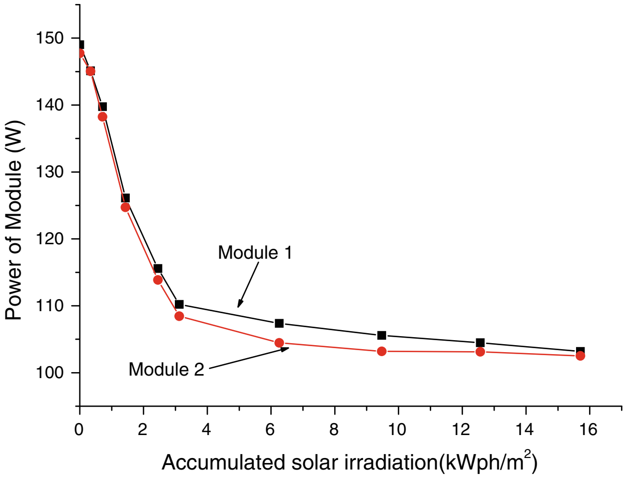

Fig. 3 The result of light-induced degradation of the above modules

degradation of Module 2 is −30.3%. However, the rate degradation of normal modules made by solar cells from polysilicon of the Siemens process is less than 3% under the same solar irradiation.

It is well-known that crystalline silicon modules have a slow power degradation (0.5–1.0% per year) [10], but the modules made by solar grade mono-crystalline silicon solar cells from a metallurgical process route do not follow this rule. From Fig. 3, we note that the modules show the rapid initial light-induced degradation of power due to the boron–oxygen metastability [11]. The mean degradation rate is about 30% in the initial days. We also find that the operation temperature of such modules is 15–22 °C higher than normal modules under the same operation conditions. This is because the reverse current of such cells is bigger than normal silicon solar cells, and more mismatch caused by different light-induced degradation rate. As indicated by other authors [12–14], the solar grade silicon feedstock from a metallurgical process route has to be improved farther so as to it can be used in photovoltaic industry. We suggest that the modules made by solar grade mono-crystalline silicon solar cells from a metallurgical process route can not be sold in the photovoltaic market.

Conclusions

Using an industrial screen-printing cell process, the efficiencies of 14% have been demonstrated on solar cells for 100% SoG-Si feedstock from a metallurgical process route. The efficiency degradation of solar cells under natural sunlight is significant, and the electrical uniformity of small cells diced from the whole cell is too bad. The operating temperature of the cells of the modules is 15–22 °C higher than normal modules under the same conditions. The photovoltaic systems are being marketed for grid-tied residential use and for building integrated photovoltaic applications. Owners, intent on being able to “sell back” power to their local utility, have expectations that may be affected by module degradation. These modules degradation can significantly degrade the operation performance of the entire system. Therefore, the modules made by solar grade mono-crystalline silicon solar cells from a metallurgical process route can not be sold in the photovoltaic market.

Additionally, this article suggests that the onset and progression of degradation need to be studied to gain a more comprehensive understanding of module degradation.

Acknowledgements The authors wish to express their gratitude to Solarfun Power Holdings Co., Ltd., and Zhejiang ERA Solar Energy Technology Co., Ltd., for their helps. This study was supported by the fund of Applied Materials Co., of USA under the Project no. XA-AM-200901.

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