SOLAR GRADE SILICON *VERSUS* ELECTRONIC GRADE SILICON FOR PHOTOVOLTAIC APPLICATIONS

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One of the most intriguing questions still remaining in photovoltaic research concerns whether silicon of a grade lower than electronic can be a valuable alternative for photovoltaic applications.

The original argument advanced in favour of "solar grade" silicon was that, the cost of silicon being related to its purity alone, ranging from 1 $/kg for the MG grade to 100 $/kg for the semiconductor grade, if some intermediate degree of purity could be shown to be suitable for medium efficiency solar cells, the cost of the material should be intermediate between that of MG silicon and that of electronic grade (EG) silicon (see Fig. 1). This argument, which was also adopted by the author in the past [1] appears, on more careful consideration, to be incorrect on two counts:

(i) there is no reason why the cost of silicon should be a monotonic function of its purity;

(ii) a threshold for low cost grades could well exist, depending on the purification procedures adopted and on the nature of the silicon feedstock.

As an example, the purity of a low grade of silicon obtained from the carbothermic reduction of quartz (MG silicon) is quite different from that obtained from the aluminothermic reduction of quartz (Al-MG). As can be seen in Tables 1 and 2, these materials, after leaching with acid to remove soluble impurities, contain different residual impurities; in the case of MG silicon the major problem is the removal of boron, phosphorus and carbon, while in the case of Al-MG silicon the removal of aluminium and carbon is the major concern.

Carbon removal from silicon is mandatory because carbon levels greater than the saturation values (about 90 at.ppm in the liquid) cause silicon carbide segregation which is known to degrade the $p-n$ junction of solar cells. Furthermore, silicon carbide particles in the liquid silicon charge, always present in silicon melts obtained from MG silicon, imply the requirement for a double Czochralsky pulling to obtain usable silicon ingots [3]. This excludes high-carbon silicon prepared from MG feedstock from the market due to cost alone.

Boron, phosphorus and aluminium, on the other hand, behave as shallow acceptor or donor levels in silicon and, at the concentrations reported in Tables 1 and 2, result in a substantial degradation of the lifetime of the minority carriers, associated with a solar cell efficiency drop to negligibly low values.
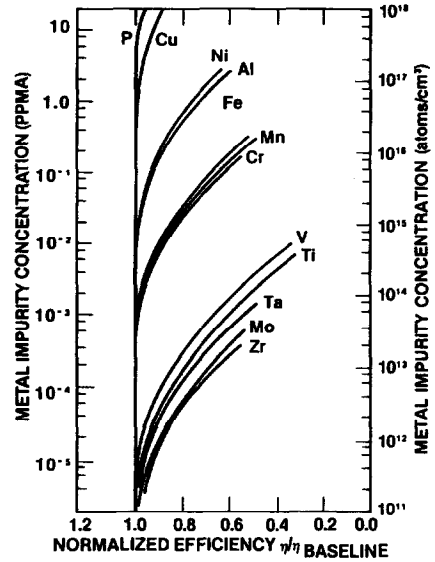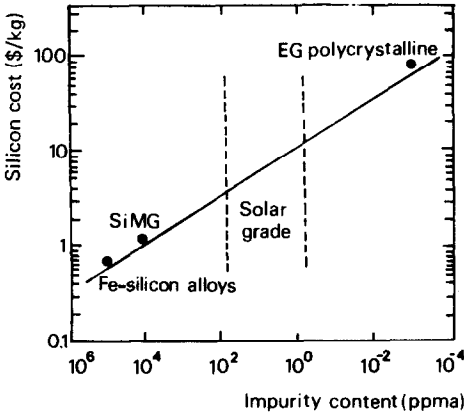
Fig. 1. Cost of different grades of silicon in relation to the impurity content.

Fig. 2. Effect of concentration of single impurities on single crystal silicon.

TABLE 1

Impurities (ppm by wt.) in MG silicon materials from different suppliers [2]

Element	A	B	C	C (acid leached)
Mn	260	500	350	< 1
Cr	25	20	17	0.05
Cu	25	50	21	1.5
Ni	110	30	25	< 0.6
Fe	3800	3500	1800	5
Al	1600	2400	1500	20
Ca	2700	2200	1450	4
Mg	60	50	45	0.5
Ti	150	250	250	0.2
B	10	20		*
P	40	30		*
V	nd	nd	12	< 0.04
Zr	nd	nd	20	< 0.2
C	**	**	**	**

*Boron and phosphorus concentrations remain essentially unaltered after acid leaching.
**Carbon content is not reported, but our experience indicates that the carbon level in MG is in the range 100 - 300 ppm by wt. and cannot be removed by leaching.

TABLE 2

Impurity concentrations (at.ppm) in Si from aluminothermically reduced quartz sand [2]

Element	Si platelets	Milled and leached
Mn	≤ 2	< 1
Cr	≤ 2	< 1
Cu	≤ 2	< 1
Ni	≤ 2	< 1
Fe	1 - 3	< 1
Al	2000 - 4000	~ 300
Ca	≤ 2	< 1
Mg	≤ 2	< 1
Ti	≤ 2	< 0.1
B	≤ 3	< 3
P	3 - 5	< 0.5
C	< 120	< 120
S	~ 1	≤ 1

Furthermore, the degree of purification (or the purity of the feedstock) depends on the threshold concentration of the impurities, above which the efficiency of the solar cells degrades to less than 80 - 90% of the baseline*, depending on the balance of the costs of the cell and of the system. As compensation phenomena could play a relevant role due to pairing, clustering, gettering of intrinsic or extrinsic defects such as isolated point defects or defect clusters, dislocations, grain boundaries and oxygen precipitates [4], the threshold concentration of the impurities could well be different from that already established [5] for single impurities in single crystal silicon (see Fig. 2).

It follows, for example, that while in single crystal silicon the deep level impurities should lie in the 10^{13} - 10^{14} atoms/cm^3 range as in EG silicon, in coarse grained polycrystalline silicon** segregation of impurities at grain boundaries, and oxide or carbide formation (depending on the heat treatment and oxygen or carbon contamination) could widen or narrow, at least to some extent, the solar silicon specifications [6]. Consequently, the use of a low grade silicon feedstock would require the development of a purification process involving, possibly, pyrometallurgical, chemical, and fractional crystallization steps, each capable of selectively removing impurities while permitting the establishment of impurity compensation phenomena, if favourable. However, if all these steps should be shown to be necessary to arrive at material of the required purity, the final cost would hardly be competitive with that of EG silicon.

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*As the baseline one uses the efficiency of a solar cell fabricated with single crystal electronic grade silicon.

**This type of polycrystalline silicon is generally obtained by chill casting or directional solidification of a molten silicon charge and permits the manufacture of ≥10% efficient solar cells.

It seems therefore no longer to be a matter for concern whether "solar silicon" is a material of lower grade than electronic silicon or whether one can foresee a unique definition for "solar grade" silicon. We are actually concerned with the possible development of a low-cost upgrading process, which would be at least competitive with the Siemens process used for the manufacture of polycrystalline silicon for semiconductor applications, with production costs (disregarding profit) of around 20 - 25 $/kg.

In spite of the difficulties, this problem is a challenge for a number of reasons. If successful, one would expect a revolutionary development in solar silicon business, with possible feedsback into the electronic market. If unsuccessful, it will have been demonstrated that, without question, no alternative exists to the already well-established Siemens process for semiconductor-grade silicon production, and that future development of photovoltaics should rely on semiconductor materials different from crystalline silicon.

In either case, however, our knowledge of the behaviour of impurities in silicon will, as a result, be dramatically improved, permitting a higher degree of confidence in the design and fabrication of semiconductor devices.

It is expected that within the next two years the photovoltaic community will be able to provide reasonable answers to all the questions raised in this paper.

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