

Preparation of polysilicon from rice-husk

The importance of crystalline silicon which is used worldwide for 90% of photovoltaic systems was presented recently¹. The conventional Siemens process to produce polysilicon involves carbo-thermic reduction of SiO₂ ($T > 2000^\circ\text{C}$) followed by chlorination, fractional distillation and pyrolysis of trichlorosilane SiHCl₃ (TCS). As this process is energy-intensive, efforts have been made to develop alternative lower energy processes. Growth of single crystals from polysilicon by the Czochralski (CZ) technique is also slow and energy intensive. It is important to reduce the total energy input to decrease the 'energy payback time' (EPT) of photovoltaic systems. The cell conversion efficiencies are also important determinants of EPT. Commercially CZ-grown single crystal modules are capable of 18% efficiency compared with multi-crystalline Si solar cells with ~16% module efficiency. The latter are produced by directional solidification techniques which are attractive because of higher throughput, faster processing and lower wastage due to wafer cutting.

There has been considerable interest in exploring readily available alternative starting materials for preparing semiconductor-grade silicon. Rice-husk appeared to be an attractive source material as it contains 10–12% silica (SiO₂) and has low metal impurity content. In the aftermath of the oil crisis of 1977, projects were undertaken at IIT Kharagpur to examine the feasibility of using rice-husk. Silica can be extracted relatively easily by burning the husk in air to obtain 'white ash' (~96% silica). This was first reported by Basu *et al.*²; one of their objectives being to provide a method of

disposing of rice-husk, which is an agricultural waste product. The work² involved chlorination of the silica (white ash) according to the Siemens process. Rice-husk cannot be used as animal feedstock while its use as a fuel leads to environmental pollution. The composition of white ash is given in Table 1. It is seen that there is considerable variation in the composition depending on the type of soil and the variety of rice.

Amick³ studied the process of anaerobic burning of rice-husk to obtain a mixture of silica and carbon. This carbon was used for carbo-thermic reduction of silica which required temperatures higher than 2000 K. There was no report of Si ingots being produced by this author. Hunt⁴ showed (Figure 1) that there were at least 20 possible metals for which the reduction reaction of silica to silicon is thermodynamically feasible. These include Li, Be, Ca, Mg, Sr, Ba, Sc, Y, Ti, Hf, Al, Ga, In, Ce and Lu. Of these Sc, Hf, Ce and Lu are expensive rare-earths while the cost factor rules out Li, Be, Ga and In. Acharya *et al.*⁵ used Mg reduction to produce silicon powder but the highly exothermic reaction is difficult to control and the imported high purity Mg was more expensive than Si.

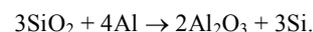
In our work the rice-husk was first pyrolysed in air at ~500°C with constant stirring such that the carbonaceous part (mainly lignin) was burnt off as oxides of carbon. This resulted in 'white ash' of grain size ~5–10 μm. This was subjected to repeated leaching in HCl and washing in deionized water to remove soluble impurities. The principal impurities after leaching were B, P, Ca and Mg.

A second source studied was quartzite rock obtained from Purulia which was

broken up and pulverized to produce fine powder with a particle size distribution between 5 and 25 μm and a maximum size of 12 μm. The impurities in the fine powder were determined by atomic absorption spectroscopy. Results indicated that Fe, Cr and Ni were the most prominent impurities at >2 ppm level. These are undesirable because they give rise to mid-gap recombination centres in Si. Interestingly the quality of the silica from the two sources could be differentiated on the basis of colour, rice-husk silica being sparkling white while the quartzite silica had a brownish tinge. Due to higher impurity content in silica from quartzite, this material was not used for further processing.

Initially using the Mg reduction process small silicon ingots prepared by Bose *et al.*^{6,7} were found to be *n*-type due to excess P and had an electron concentration of $3 \times 10^{17}/\text{cm}^3$ with electron mobility of 210 cm²/V.s. The principal impurities detected by mass spectrometry for P, C, B and Al were between 80 and 10 ppm (Table 2).

However from cost and availability considerations aluminothermic reduction of SiO₂ appeared to be more favourable using commercial grade Al from an Indian source. This reduction process for quartzite sand was reported by Dietl *et al.*⁸. The free energy diagram for aluminothermic reduction of SiO₂ is shown in Figure 1. The exothermic reaction is given by



Reduction was conducted in a pit furnace in a nitrogen atmosphere (Figure 2). The white ash was introduced into the

Table 1. Composition of white ash (silica)

Compound	SiO ₂	K ₂ O	Na ₂ O	MgO	P ₂ O ₅	CaO	SO ₃	Cl	Fe
Percentage	86.9–96.3	0.58–2.5	0–1.75	0.12–1.96	0.2–2.85	0.2–1.5	0.1–1.13	tr–0.42	tr–0.56

tr, Trace.

Table 2. Mass spectrometric analysis of Mg-reduced Si from rice-husk

Element	B	C	Na	Mg	Al	P	Ca	Ti	Cr	Mn	Fe	Cu	K	O
Conc. (ppm)	10	20	6	6	10	78	2.3	nd	1	1.8	nd	7.9	1	1.3%

nd, Not detected.

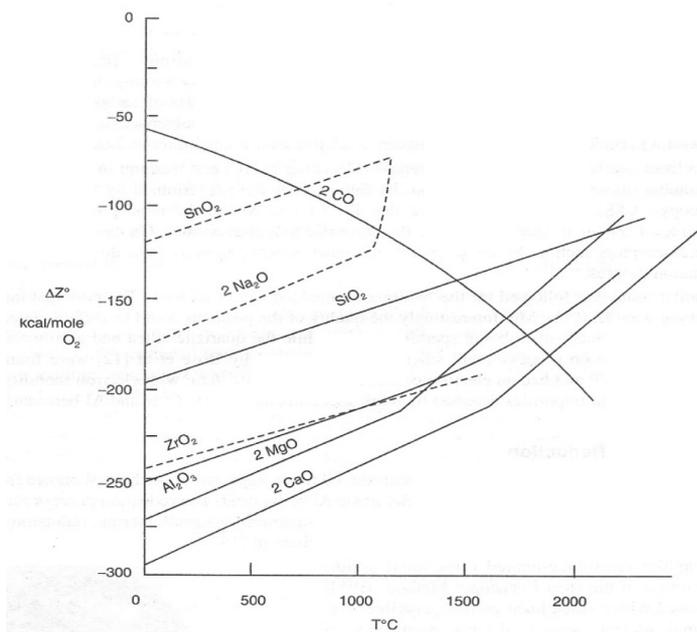


Figure 1. Free energy diagram for metallo-thermic reduction of SiO_2 .

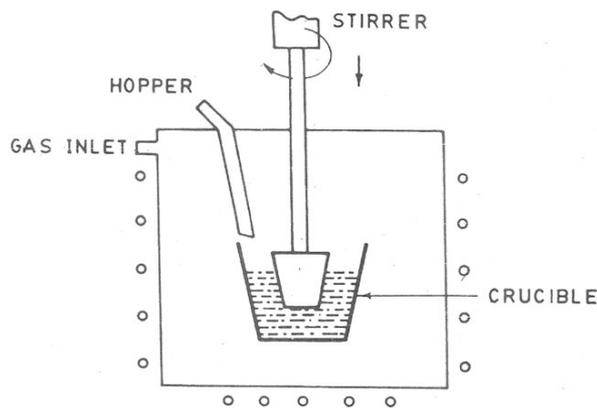


Figure 2. Alumino-thermic reduction.

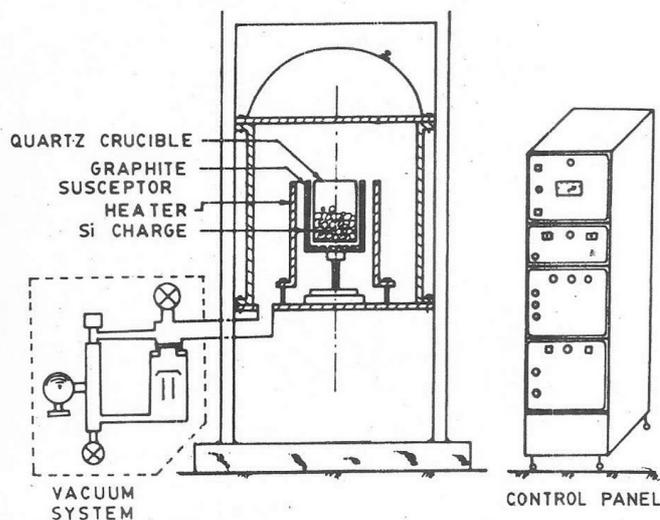


Figure 3. HEM furnace for directional solidification of silicon.

$\text{Al-Al}_2\text{S}_3\text{-SiO}_2$ slag through a hopper. The Al_2S_3 was produced *in situ* by introducing S. The slag composition was varied and the reduction temperature was optimized to 1060°C . Continuous stirring of the melt using a ceramic stirrer aided the reaction as a result of which small Si platelets were formed which are collected for grinding and acid leaching.

For preparation of Si ingot, a high vacuum graphite resistance-heated furnace of the Heat Exchanger Method (HEM) with a silica-lined graphite crucible was used for directional solidification (Figure 3). This process of HEM growth had been perfected by Khattak and Schmid⁹. Pre-melted small Si nuggets were used as compaction of fine powder proved difficult. Using this technique 4 inch diameter silicon ingots (Figure 4) were grown¹⁰ having grain size between 2 and 5 mm as required for efficient multi-crystalline solar cells. Due to the use of Al as the reducing agent, the ingot resistivity was found to be rather low ~ 0.04 ohm-cm with hole concentration of $3 \times 10^{18}/\text{cm}^3$ and hole mobility of $50 \text{ cm}^2/\text{V.s}$. This amounted to ~ 60 ppm Al which could be reduced further by directional solidification as the distribution coefficient of Al in Si is 1.8×10^{-3} . With slagging the resistivity was increased to 0.08 ohm-cm; Secondary Ion Mass Spectrometry studies showed that this was mainly due to reduction of Al and also B, K and Ca. Al acts as a shallow acceptor in silicon with an ionization energy of 0.056 eV and is acceptable as it results in p-type conductivity as used as the base layer in solar cells.

A multi-crystalline sample of Si was used as a photoelectrode in a photoelectrochemical (PEC) solar cell. While a single crystal sample gave an open-circuit voltage $V_{oc} \sim 400$ mV, under identical conditions the sample obtained from rice-husk gave $V_{oc} \sim 250$ mV. From I-V characteristics the grain boundary height was found to be 0.056 eV which decreased on hydrogen passivation, suggesting the presence of O at the grain boundaries.

The feasibility of alumino-thermic reduction of white ash was demonstrated in these experiments. Large grain multi-crystalline Si ingots were thus prepared by directional solidification. Recently a company in California¹¹ has reported the use of 'rice hulls' by carbo-thermic reduction to obtain solar-grade silicon. The report claims to reduce the energy input to 50 kWh/kg from 200 kWh/kg in the



Figure 4. Four inch diameter multi-crystalline Si ingot from rice-husk (adapted from ref. 10).

Siemens process. Alumino-thermic reduction should require even less energy due to the considerably lower temperature of reduction. Further reduction of Al content is required by slagging or directional solidification.

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Uranium mineralization in Palaeoproterozoic Khetabari Formation, Bomdila Group, Sie-Rimi area, West Siang district, Arunachal Pradesh

The Palaeoproterozoic low-grade meta-sedimentary rocks of Bomdila Group, Arunachal Pradesh, occurring as a NNE to NE trending belt in the easternmost part of the Lesser Himalaya have been recognized as favourable hosts for uranium mineralization. Its basal subdivision, the Khetabari Formation having ferruginous, calcareous quartzitic meta-sediments, graphitic/carbonaceous phyllite, minor carbonates, chert and paramphibolite and garnetiferous psammopelites is bounded by the Permocarboneous Gondwana equivalent Miri quartzite in the east and with the 1.9-Ga-old intrusive Bomdila/Ziro Gneisses in the

west. The rocks of the Khetabari Formation show multiple episodes of deformation. The F_1 folds usually identifiable in the psammitic rocks of the Khetabari Formation are of isoclinal geometry. The most pervasive planar fabric S_1 is developed parallel to the axial plane of the F_1 folds and in most places parallel to the S_0 plane (original bedding plane), except near the hinges. The F_2 folds dipping at moderate to steep angles towards SE developed during the subsequent deformation are superimposed over F_1 . Co-axial refolding of the F_1 folds producing crenulation cleavage (S_2) is found generally in the limbs of the isoclinal folds

within quartzo-feldspathic schists¹. Effect of ductile shearing within the psammo-pelites of the Khetabari Formation is evident by the presence of asymmetric quartz porphyroclasts having long tail, sigmoidal-shaped quartz laminae in the schistose portion, pinch and swell of quartz grains, etc.

Exploration efforts over three decades have resulted in locating about 200 uranium occurrences in a variety of rocks mainly of Palaeoproterozoic age. Conspicuously, uranium mineralization in all these lithounits is invariably associated with sulphides. Sericitization, chloritization, hematitization and silicification are