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A Low Cost, Low Energy Route to Solar Grade Silicon from Rice Hull Ash (RHA), a Sustainable Source

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Abstract

Polycrystalline silicon, with impurity levels lower than those of the SEMI III standard for solar grade silicon feedstock (≈ 99.9999 % pure), was produced using rice hull ash (RHA) as a biogenic silica source. The RHA is first purified using very simple, low cost, low energy, acid milling/boiling water wash purification steps and pelletization followed by carbothermal reduction using an experimental 50 kW electric arc furnace (EAF) operated at 1700-2100 °C in batch mode. Typical processing involves adding 3.6 kg of pellets to the EAF followed by introduction of an additional 3.6 kg charge every 6 h after the start of carbothermal reduction. This approach produces up to 1.4 kg of silicon per batch. Purities, determined by inductively coupled plasma optical emission spectrometry (ICP-OES), were reproducibly found to be 99.9999 wt. % (6Ns) with B contents of ≈ 0.1 part per million by weight. This process escapes multiple process steps including the intermediacy of metallurgical grade silicon and the production and reduction of chlorosilanes as currently used in the Siemen's process. Furthermore, burning rice hulls to produce electricity and RHA, generates more energy than required for the overall process.

Finally, the carbon footprint for the process discussed here is very low. The rice plant "fixes" CO_2 as it grows. The recovered hull contains sufficient amounts of this carbon that it can be burned to generate electricity returning part of this carbon to the atmosphere as CO_2. The carbon retained in the RHA

is still from fixed CO_2 and provides the carbon source (especially in the Path 2 process) for carbothermal reduction returning the remaining carbon to the atmosphere as CO_2. A further point is that the alternative of landfilling with RHA or especially rice hulls would lead to generation of methane, a known green house gas. Thus, one might even argue that the carbon footprint for the process described here is actually negative.

Introduction

The primary limiting factor in the widespread use of photovoltaic cells is the high cost of the electrical energy they produce compared to more traditional sources. This is mostly due to their high manufacturing costs. It is estimated that 45% of the cost of a traditional solar panel comes from the silicon used.[1] In terms of cost, the best wafering technologies offer the potential to reach ≈ 6 g Si_{pv}/watt (from current averages closer to 8^{+}g/watt).[2] New technology, such as kerfless wafering offers the potential to drop to < 1 g/watt but is not used commercially at present.[3] In 2008, the spot price of polycrystalline silicon rose to \$450/kg, while prices have since dropped to ≤ \$22/kg.[4]

Although industry has invested billions of dollars to meet this ever-increasing demand, the technology to produce Si_{pv} remains largely unchanged requiring the energy intensive, and chlorosilane dependent Siemens process or variations thereof.[5] Another detrimental aspect of current Si_{pv} production is the amount of energy required to produce high purity polycrystalline silicon via the Siemens process or slightly more energy friendly industrial processes (e.g. fluidized bed technology[1b]). While great improvements have been made, state-of-the-art plants still use ≈ 75 kWh/kg Si purified.

The impetus for the work conducted here derives from a 1980 Exxon/Mobil Patent and several publications thereafter by Amick et al targeting the use of rice hulls (RHs) as a starting point for the direct production of photovoltaic grade polysilicon, Si_{pv}, via reaction (1) below.[6]

The motivation for using plant derived biogenic silica, comes from the fact that all plants (to some extent) extract SiO_2 from the soil while naturally filtering out most heavy metals. In particular, grasses including rice, wheat, oats and barley have high concentrations of SiO_2 in their hulls, husks or stalks.[7]

For example rice hulls, removed at centralized rice milling plants, contain 15-20 wt. % amorphous SiO_2. In the U.S., rice production runs to million ton/yr quantities that are milled with coincident production of 20 wt. % rice hulls (commodity scales).[8] The hulls are frequently burned as a biomass fuel or simply to reduce their volume for disposal generating rice hull ash (RHA). The resulting RHA contains 65-90% amorphous, high surface area SiO_2 with the remainder being amorphous, high surface area carbon and some mineral content (see Table **1**). The plant pre-purifies the SiO_2 through selective uptake greatly reducing the various contaminants typically found in SiO_2 sources.[1b] Consequently, RH and RHA are much purer than feedstock C and SiO_2 sources used to make metallurgical grade silicon, Si_{mg}.[9] The traditional reactions involved in the production of polycrystalline silicon:

$$SiO_2 + 2C \xrightarrow{1900°C} 2CO + Si_{mg} \text{ (mg = metallurgical grade)} \quad (1)$$

$$Si_{mg} + HCl \xrightarrow{\text{Cu/Sn catalyst/300°C}} HSiCl_3 \text{ and/or } SiCl_4 \quad (2)$$

$$4HSiCl_3 \xrightarrow{\text{disproportionaton catalyst}} SiH_4 + 3SiCl_4 \quad (3)$$

$$H_2 + HSiCl_3 \text{ (or } SiH_4) \xrightarrow{\text{hot wire/rod}} Si + HCl \text{ (recycled)} \quad (4)$$

The work of Amick et al strongly suggests the potential to escape the chlorosilane processing steps (Siemens Process) and rely solely on reaction (1) because one can pretreat the RH (RHA) to reduce impurity contents to those acceptable for Si_{pv}. The use of RHA instead of RH has several advantages at laboratory and industrial scales: processing of RHA during purification is less costly in terms of volumes of RHA handled, volumes of liquids (acid and water washes) and thereafter extent of drying required before the electric arc furnace (EAF) process and the volumes of blanket gases used in the EAF. Furthermore the size of EAF needed is greatly reduced. Finally the conversion of RHA into silicon avoids the costly and high temperature RH carbonization step used by Amick et al before carbothermal reduction. At this juncture, it is important to point out that the Amick efforts never resulted in the actual production of high purity silicon from RHs only suggested its possibility.

The objectives of the research reported here were to: (1) develop a low cost, low energy process for purifying RHA, (2) convert the purified RHA into polycrystalline silicon using carbothermal reduction, and (3) control the impurities during the whole process to meet or exceed the standards for solar silicon feedstock (SEMI III).[10]

Results and discussion

The general objective of the work reported here was to explore replacing RH with RHA as a means of generating high purity silicon (≈ 6Ns purity) while avoiding routes that rely on Si_{mg} and chlorosilanes. In this work, we pursued a batch rather than a continuous process as being easier to scale at very small scales. We were surprised to find that designs for small-scale silicon EAFs were not available in the literature and we were therefore forced to design and engineer our own culminating in the Figure **1** design as realized in Figure **2**, which shows it both partially loaded with 3.6 kg of pelletized RHA (see below). The overall size of the furnace is 50x50x75 cm, see Figure **2b**. The carbon crucible has an ID of 21.6 cm and a depth of 23 cm. The furnace can produce up to 1.6 kg of silicon within 24 h as discussed in more detail below.

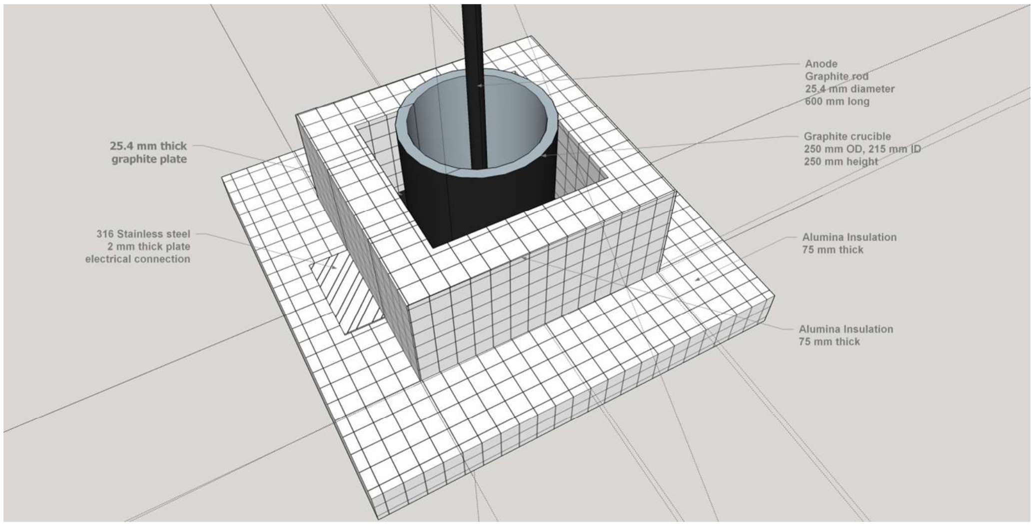

Figure 1. Schematic of Home-Built DC 50 kW EAF. Top cover is not shown, during operation zirconia grit is added to fill cavity between crucible and alumina insulation.

Figure 2a. Interior of the EAF with 1/3 of the feedstock loaded. **b**. EAF in operation, 50x50x100cm.

A further objective was to carefully analyze the materials at each process step. It is important to note that the Al and Fe impurities were the most difficult to remove. Finally, removal of samples for analyses was found to also be a challenge as the removal process itself introduced impurities not in the sample itself. The following provides a brief overview of the purification steps.

Purification. As shown in Table **1**, the most important impurities extant in unpurified commercial RHA are potassium, calcium and phosphorous. While impurity removal in RH as done by Amick required concentrated acids (18.5 wt.% HCl), the impurities present in RHA are quite soluble in dilute acid (3.7 wt. %). Table **2** demonstrates that the impurities present in RHA are easily removed. As-received RHA was initially analyzed by glow-discharge mass spectroscopy by the Evans Analytical group. Results were confirmed in-house by ICP-OES, see experimental.

Table 1. Impurities in typical as-received RHA batch (carbon not included).

Impurity	Al	B	Ca	Cr	Cu	Fe	Li	Mg	Mn	Ni	K	Na	Ti	P	Zn	Total ppmw
ppmw	340	16	1200	<1.0	4.8	350	-	750	260	-	11400	260	0.2	2100	50	16732

Table 2. Impurities in RHA during the various process steps of Path 1 (“-“not detectable)[a]

Impurity (ppmw)	Al	B	Ca	Cr	Cu	Fe	Li	Mg	Mn	Ni	K	Na	Ti	P	Zn	Total ppmw
RHA raw	340	16	1200	<1.0	4.8	350	-	750	260	-	11400	260	0.2	2100	50	16732
After milling	140	5	190	<1.0	1.2	240	-	210	60	-	1300	35	-	10	0.3	2193
After hot wash	64	4	45	<1.0	0.5	45	-	32	20	-	80	5	-	-	-	297
After BWW[b]	12	2	21	-	-	14	-	8	8	-	10	3	-	-	-	78
Full Process	1	1	11	-	-	2	-	5	2	-	6	3	-	-	-	31

a. Note that many of these impurities are eliminated during EAF operation. b. Boiling water wash.

Acid milling removes most impurities efficiently, but one important aspect is that impurities dissolved in acid solution can re-adsorb.[11] Water washes after milling remove re-adsorbed species, often in amounts comparable to those initially removed by milling. Also while RHA contains significant phosphorous as phosphates,[12] its high solubility in dilute acid reduces its presence below detectable levels early in the process. Potassium is present as a mixture of potassium oxide, hydroxide and carbonate. All three compounds are very soluble in dilute acid.

In addition to requiring much less concentrated acid,[6] purification of RHA instead of previous work done with RH is much more cost effective. Per unit of silica purified, RHA purification needs 5 times less acid. At equivalent size, processing equipment can purify RHA at 5 times the rate of RH. Additionally RH acid extraction leads to a wet product that must be dried prior to conversion to RHA consuming more energy resulting in a significant loss of net energy.

Carbothermal reduction. As expected from the literature, the efficiency of carbothermal reduction of silica to silicon is highly dependent on the physical size of the reactor.[1,13] Most silica present in purified RHA is lost to gaseous SiO and the small reactor size does not allow for this SiO to condense back into the reactor as it does in an industrial sized system. The highest yields were obtained by partially filling the reactor with the feedstock (the arc was unstable if the reactor was empty), then adding the rest in several increments. The specifics of each run are detailed below.

The run that had the highest yield produced 1.4 kg of silicon from 10.9 kg of RHA (dry weight) of Path 1 pellets ($C:SiO_2$ ratio 1:1.65, see below). One-third of the pellets were placed in the crucible, then the arc was started at 4 kW and increased to 15 kW after 30 min. A uniform but somewhat higher than normal operating temperature (temperature could only be measured reliably at the bottom exterior of the crucible: 2015-2040°C vs 1850-1930°C for standard operation) was reached after 5 h and 12 kW was required to keep the temperature stable.[1,13] Another third of the pellets was added after 10 h with the final third added after 16 h. The total run time was 22 h and gave ≈ 1.4 kg of silicon (37% of theoretical yield). As seen in Table **3**, the purity was low. Nonetheless the yield was much higher than expected at this scale. It should be noted that the actual reaction mechanism for the carbothermal reduction of silica by carbon is much more complex than reaction (1) shows. Reaction (5) is one of the rate-limiting components of reaction (1).

$$SiO_2 + C \xrightarrow{1700°C} CO + SiO_g \qquad (5)$$

The use of carbon deficient purified RHA as feedstock requires the addition of some graphitic carbon at the submicron scale via thorough pre-mixing (see below) to adjust the C:Si ratio. The rates of solid-state reactions are dictated by solid-state diffusion rates and distances. The time to complete the

Table 3. Impurities in selected batches compared to SEMI II standard (O, C not included), ("-" not detectable).

ppmw	Si impurities Highest yield	Si impurities Best Path 1	Si impurities silicon from melt Best Path 1	Si impurities Best Path 2	SEMI III
Al	34	0.1	-	0.4	0.3
B	2	-	-	-	0.1
Ca	0.3	0.1	-	1.6	0.1
Cr	-	-	-	-	0.2
Cu	-	-	-	-	0.2
Fe	5	0.2	-	3.6	0.2
K	0.5	0.05	-	1.7	0.1
Mg	2	0.05	-	0.6	0.1
Mn	4	-	-	-	0.2
Na	0.5	0.02	0.05	1.2	0.1
P	-	-	-	-	0.05
Purity	99.99%	99.9999%	99.99995%	99.9990%	99.999%

reaction is controlled solely by the distance species in the largest particles must travel (diffuse) to reach the reaction zone (typically at the particle surface). Hence the larger the biggest particles are, the longer time it takes to get complete reaction. The following empirical formula, Equation (1), can be used as a guide to predict reaction times for solid-state reactions.[14]

$$[1 + (\mathbf{z}\text{-}1)\mathbf{x}]^{\frac{2}{3}} + (\mathbf{z}\text{-}1)(1\text{-}\mathbf{x})^{\frac{2}{3}} = \mathbf{z} + 2(1\text{-}\mathbf{z})\frac{\mathbf{Kt}}{\mathbf{r}_{\mathbf{A}}^{2}} \tag{1}$$

It describes the time required for reactant A particles of radius r_A and mole fraction x, to react given a global rate constant K_t for reaction, where z is the unit volume of product formed from a unit volume of A. The latter accounts for changes in density. This formula is a relatively crude method of predicting solid-state reaction times because it does not consider phase changes, or impurities in primary particles, or aggregates. It does suggest that the production of SiO_g, should be faster when using RHA then by using the usual quartz and coal feedstocks. However, to be most useful in predicting reaction rates, it is important to recognize that one must use the diffusion coefficients for the reactants and the reactant products.

Si, O and C elemental mapping was done of the purified RHA to confirm the nanometer scale mixing of the SiO_2 and C in RHA. Figure **3** shows a scanning tunneling electron microscope image of a

RHA sample. The particle sizes are of the order of 20-50 nm. Figures **4-6** show elemental maps of the silicon, carbon and oxygen in the Figure **3** sample all of which suggest that all the elements are relatively homogeneously dispersed confirming the intimate (nanoscale) mixing of the amorphous SiO_2 and C in the RHA.

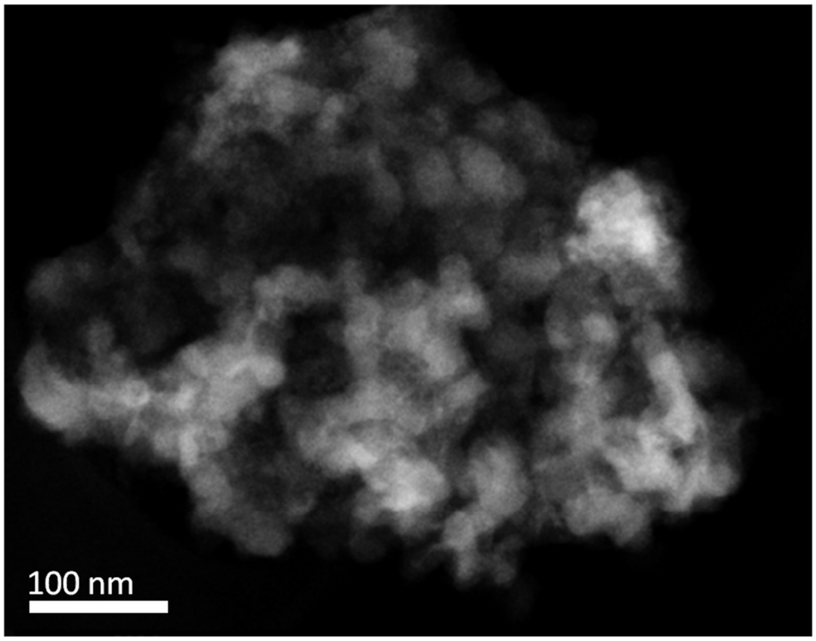

Figure 3. STEM picture of RHA sample.

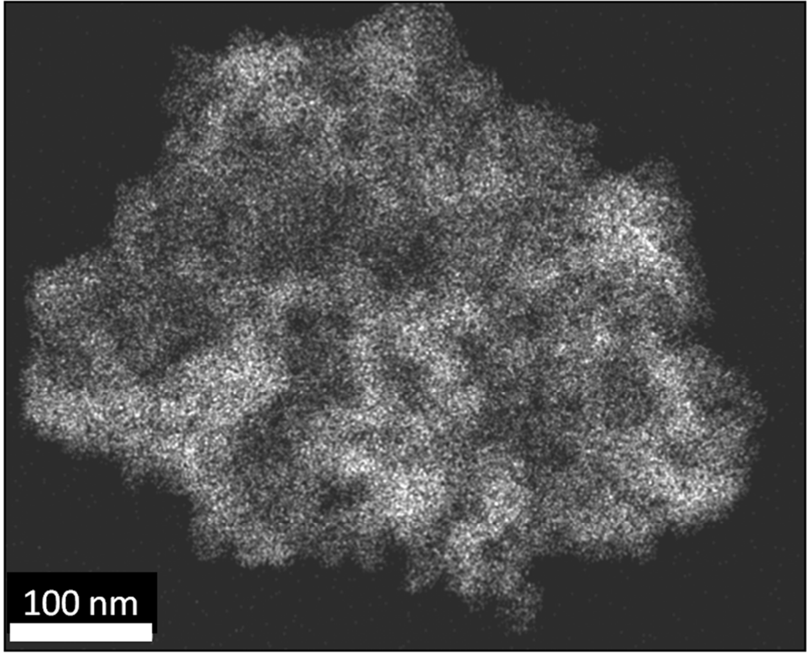

Figure 4. Silicon mapping of RHA sample shown in Figure **3**.

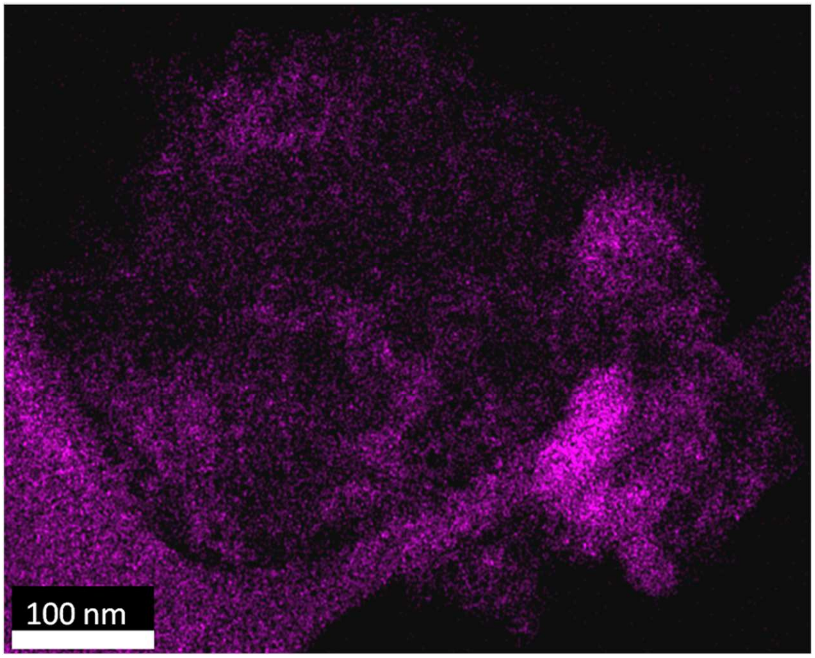

Figure 5. Carbon mapping of RHA sample shown in Figure **3**.

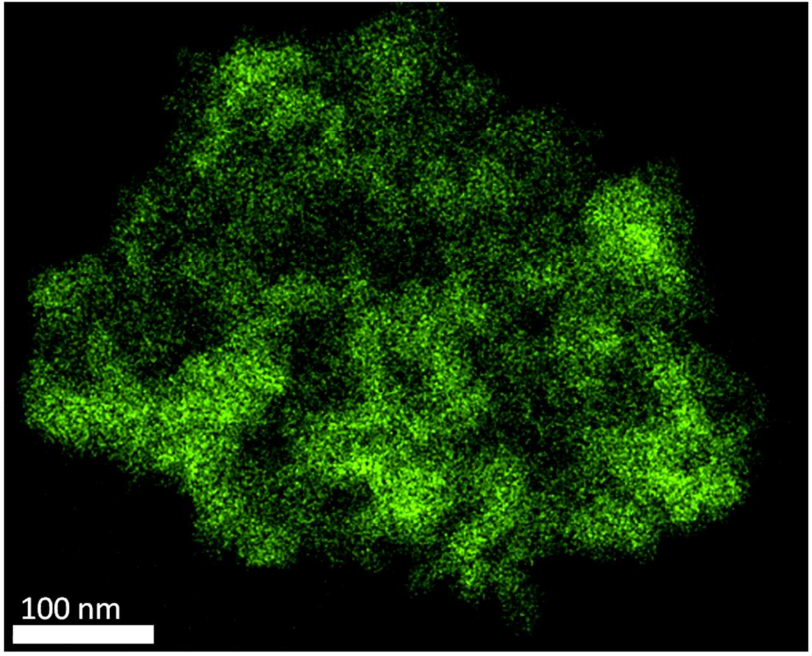

Figure 6. Oxygen mapping of RHA sample shown in Figure **3**.

This intimate mixing results in very much smaller diffusion distances: the time to complete the transformation to silicon should be much faster than in traditional EAF processing of Si_{mg} meaning high throughput in a continuous reactor and or the potential to use a smaller EAF and less electricity to produce identical amounts as the processing times are reduced.

In a small scale EAF most of SiO_g leaves the reaction zone thereby limiting product yields.[1b,13] In our case, the high concentration of SiO_g in the reactor results in some of it condensing back into the reaction zone, as occurs in larger reactors. This explains the higher than expected yields. The high rate of SiO_g production probably also explains the high rate of conversion of the RHA to silicon. The rate of purified RHA consumption in the system is roughly 4x the rate expected compared to typical quartz/coal feedstock. Even though currently the carbothermal reduction of silica to silicon only represents a small fraction of the price of final Si_{pv} (Si_{met} only costs \$3/kg), a faster rate of conversion has some benefits. If these results are confirmed at industrial scales, energy losses as well as the amortizing cost of the capital equipment per kg of Si produced will be lowered.

The run that gave the highest silicon purity (6Ns) had a yield of 550 g (16% of theoretical yield): Initially 3.76 kg (dry weight) of purified and carbon adjusted RHA pellets (using **Path 1**) were placed in the crucible, after 10 h another 3.76 kg was added, then a final 3.76 kg after 16 h. Total arc duration was 21 h at which point the arc was shut and the system allowed to cool down before the silicon could be collected. The initial setting of the arc is 4 kW, increased to 12 kW in 30 minutes. The power was reduced after 5 h to 9.5 kW to keep temperature constant (1880-1930°C). On cooling, 550 g of silicon was collected (16% of theoretical yield). Note that only the anode or carbon rod is consumed in the process, the “container” can be reused.

The purity of the silicon was determined to be 6Ns as shown in Table **3** comparing impurities to the SEMI III standard (carbon and oxygen not counted). Several other runs were done using similar conditions but different batches of RHA (some with more than twice the total amount of initial impurities) and giving silicon with 4-5Ns purities, as seen in Table **4** along with the impurities in the corresponding starting RHA.

Samples of silicon taken from our system while molten show even higher purity with sodium being the only impurity detected using glow discharge mass spectroscopy. This suggests that by scaling and improving our system, so that the molten silicon can be cast such that it undergoes directional solidification on cooling could result in even higher purity silicon as is currently done commercially.[1b]

Table 4. Impurities in selected batches compared to SEMI II standard (O and C not included) and impurities in corresponding starting RHA.

ppmw	Batch 4 RHA	Si impurities Batch 4 Second run	Si impurities Batch 4 First run	Batch 3 RHA	Si impurities Batch 3	Batch 2 RHA	Si impurities Batch 2	Batch 1 RHA	Si impurities Batch 1	SEMI III[a]
Al	350	-	-	180	0.7	350	3.5	1600	0.1	0.3
B	15	0.1	0.2	28	0.4	53	0.0	Unk	0.05	0.1
Ca	1400	0.2	0.2	840	0.3	1400	10.9	5250	0.3	0.1
Cr	<1.0	0.05	0.05	<1.0	0.5	1.2	-	Unk	-	0.2
Cu	4.6	-	-	4.6	-	8.3	-	Unk	-	0.2
Fe	340	2.0	4.3	190	12.7	330	5.6	1400	0.1	0.2
Mg	740	-	0.03	530	0.05	850	10.6	2400	0.01	0.1
Mn	260	0.2	0.5	160	1.0	240	7.5	1050	--	0.2
K	11000	0.2	0.4	10000	0.5	20000	67.3	33800	1.2	0.1
Na	260	-	-	250	-	410	2.7	650	0.4	0.1
P	2000	-	-	2100	-	5000	-	1050	-	0.05
Purity	98%	99.9997 %	99.9994 %	98%	99.998 %	97%	99.98 %	95%	99.9997 %	99.999 %*

[a]Note that SEMI III standard allows for the presence of heavy metals impurities not present in either RH, RHA or Si produced from RHA.

It should be noted that the RHA used in this study was produced by one of the most efficient large-scale RH combustion systems currently operating, resulting in higher output of energy produced and lower carbon content in the RHA than other industrial RHA facilities. In designing new systems, basing it on a best of class commercial application, designed to maximize energy efficiency is an important base line. RHA from other less efficient industrial facilities with higher carbon content, can be directly substituted in our process and will significantly reduce the amount of added graphite needed to prepare the feedstock for carbothermal reduction using **Path 1** (see experimental).

The most successful **Path 2** run produced 110 g of 5Ns silica. In this run, the RHA used to form pellets had 40 wt. % of the silica extracted (3.11 kg dry weight) and after purification was mixed with 265 g of graphite powder and pelletized. All the pellets were placed in a single batch in the EAF. Power was quickly increased from the initial 2 to 16 kW at 200 kW/min; it took 6 h for all the RHA to react. Path 2 is designed for RHA produced with much less than 26.5 wt. % carbon (i.e., RHA produced with high efficiency energy output). If the carbon content is at this level or higher, no graphite needs to be added.

Path **2** has the added advantage that it allows co-production of either glycoxysilane or spirosiloxane. These compounds have been used to make low cost, high purity precipitated or fumed silica and as such offer potential as additional revenue streams for this process at industrial scales. This path also eliminates the need for the addition of any (or very little) high purity graphite to achieve the correct Si:C ratio for carbothermal reduction thereby offering the potential for still lower production costs.

Figure 7. Typical broken silicon piece collected from EAF.

Finally, it is important to note that the RHA pellet feed consists of relatively high surface area materials. This feedstock, despite being furnace dried will pick up water on standing and the water content likely affects rates of reaction and yields. The Path 2 materials have higher surface areas than the Path 1 materials as the extracted silica increases surface areas. These materials will be of somewhat lower densities and will behave differently from the Path 1 feedstock. Thus, yields from batch to batch can vary simply because of pellet density and water content.

Conclusions

In this study we have demonstrated that RHA can be purified at low temperatures (< 200°C) using only dilute acids and hot water, due to its high reactivity. Contrary to earlier work on RH, this purification is low-energy and economically viable. At industrial scales, the energy required for purification of RHA is estimated at 5 kWh/kg of final silicon produced, much less than the 65 kWh/kg of the currently most efficient Siemens chlorination plant.[1,2] Note that the production of RHA itself from RH produces 23 kWh/kg of final silicon produced, more than the purification requires. Avoiding the use of chlorosilanes or any gaseous process during purification, coupled with this low energy requirement results in low overall CAPEX (capital expenditures) and OPEX (operational expenditures). Enpower Corp. (San Ramon, Ca.) and Harris Group Inc. (Seattle, Washington) estimated costs at 100 tons/day capacity for CAPEX at \$23-25/kg and \$5-6/kg after a 6 months study of the energy costs, chemical use, recycling and related costs.

This study was successful in using purified RHA as high purity feedstock to produce 6Ns pure silicon surpassing the SEMI III specification for solar silicon polycrystalline feedstock. Using our in-house designed and built EAF, we were able to produce up to 1.6 kg per batch, reaching an unexpectedly high 37% theoretical yield compared to literature expectations. The submicron (nanometer scale) mixing of carbon and SiO_2 in RHA during carbothermal reduction provides a reasonable explanation for both the high final yields and rapid rates of reaction. These results may suggest that the use of purified RHA at industrial scales could result in faster silicon production for a given charge while also minimizing the energy costs for carbothermal reduction.

Almost all the carbon released (as CO_2) both during RHA and silicon production corresponds to the carbon absorbed by the plant during growth. The overall process has therefore a very low carbon-footprint. It could be argued that it in fact decreases greenhouse gas emissions, as landfilled RH produces methane, a much worse greenhouse gas than the carbon oxides released to make RHA, and then silicon.

Increasing the scale of our EAF reactor is also necessary for further optimization of silicon purity and post reduction processing of Si produced. Further work would use this scale up to continue silicon refining and allows for the production of Si_{pv} boules, wafering and final testing of the Si_{pv} in an actual solar cell. In particular, scale up should lead to design modifications that allow pouring of the silicon at high temperature. This would allow for selective gradient crystallization of the silicon, selectively segregating most of the retained impurities including carbon as SiC and oxygen impurities and resulting in a final silicon with higher than 6Ns purity.[1b] This would be an ideal low cost feedstock for Si_{pv} boules.

Experimental

Unless otherwise specified all chemicals were purchased from Spectrum Chemicals, Inc. RHA was provided by Wadham Energy Inc. (Williams, CA). In particular, "trace grade" chemicals are those used as standards for ICP-OES analyses as detailed below. Typical impurity contents of the as-received RHA are listed in Table **1**.

As RHA contains only 2-20 wt.% carbon, far less than the 1:1.8 SiO_2:C molar ratio required for theoretical carbothermal reduction (Reaction 1), the SiO_2:C ratio must be adjusted either after or during the purification process. Two different paths were explored targeting high purity silicon from RHA.

Path 1

In this path, the SiO_2:C ratio is adjusted after RHA purification. The RHA purification process consists of milling the RHA in dilute aqueous acid, filtering the RHA, washing it in cold water, filtering then leaching the RHA in boiling acid, filtering then washing in boiling water and filtered one last time.

RHA milling in acid RHA (5 kg) was placed in a 25 L Nalgene carboy with 5 kg of milling media and 12 L of HCl solution (3.7 wt. % HCl). Media was magnesium-stabilized zirconia, 11 mm diameter spheres, made by TOSOH (Tokyo, Japan). The RHA was milled for 48 h.

Filtration All RHA filtrations were run through a Met-Chem Inc. (Cleveland, OH) 1-3 cubic foot, adjustable filter press. All wet parts are made of PVC with polypropylene filters. Filtration uses an air powered 2.5 cm diaphragm pump (polypropylene body with PTFE membranes) operating at 690 kPa. Once all RHA is pumped into the filter plates, the liquid was filtered off (typically 1 h), then 20 L of distilled water is pump through the RHA cakes and filtered off over a 1 h period. Filters and all wet parts are cleaned and rinsed between each step.

Acid leach Two 20 L glass reactors equipped with overhead mechanical stirring (glass stirring shaft, PTFE blades) and a reflux condenser (nitrogen) are each filled with 12 L of 18.5 wt. % HCl. The acid is refluxed for 24 h and then the reactors are rinsed with distilled water. This step ensures no impurities are leached from the reactors. The RHA (10 kg initial wt.) is split between the 2 reactors and 12 L of 6.2 wt. % HCl is added, the suspensions boiled for 16 h. The suspensions are filtered at 90 °C.

Boiling water wash Two 20 L glass reactors equipped with overhead mechanical stirring and a reflux condenser under nitrogen flow are each filled with 12 L of 18.5 wt. % HCl. The acid is refluxed for 24 h, and then the reactors are rinsed with distilled water. The RHA is then split between the 2 reactors and 12 L of distilled water is added to each, the suspensions are again boiled for 16 h and then filtered at 90°C.

Carbothermal feedstock preparation The purified RHA was analyzed by TGA-DTA to determine the exact carbon, water and silica content. Analysis was performed using a Q600 simultaneous TGA-DTA (Thermal instruments) using a 10°C /min heating rate to 1000°C under 60 mL of oxygen.

Based on the silica and carbon contents as determined by TGA-DTA; additional carbon is added as high purity graphite: 30 parts per million by weight SiO_2, all other impurities total < 1 part per million by weight (ppmw). Due to expected gaseous SiO losses in the EAF; the final SiO_2:C ratio in the feedstock is 1:1.65 instead of the theoretical 1:2. The RHA and 90°C distilled water are mixed in a 30 L polyethylene container and treated with ammonium hydroxide to obtain a pH 8 suspension. The suspension is then filtered and the wet cakes are shaped into 30 g balls while adding the graphite. The balls are then air dried at 230°C for 24 h.

Path 2

In this path, the SiO_2:C ratio is adjusted during RHA purification. The RHA purification process consists of milling the RHA in acid, filtering the RHA and washing it in cold water, neutralizing the RHA, filtering, then extracting part of the RHA silica in with ethylene glycol or some other diol and catalytic amounts of base. Once the ethylene glycol/diol/dissolved silica is filtered off, the RHA is washed in boiling water, filtered then leached in boiling acid, filtered then washed in boiling water and filtered one last time:

Milling, filtrations, leaching, neutralizing and washing are identical to the Path 1 conditions.

Silica extraction (for Path **2** processing) This reaction is detailed elsewhere.[15] In these experiments, 2.5 kg of neutralized RHA are placed in a 20 L reactor equipped with overhead mechanical stirring and a reflux condenser. Water (12 L) is added and the suspension refluxed for 24 h. The reflux condenser is replaced with a distillation condenser and ethylene glycol is added gradually to replace water distilled over. Once the distillation temperature reaches 190 °C, catalyst is added. Catalyst is prepared separately by dissolving 4 mol % NaOH (based on actual silica content of the 2.5 kg of RHA) in boiling ethylene glycol (at a ratio of 1 g of NaOH per 10 mL of ethylene glycol). Water formed during silica depolymerization is distilled out coincident with ethylene glycol during the reaction and can be recycled. After 6-20 h, 20-50% of the silica is extracted as the glycoxysilane, $Si(OCH_2CH_2OH)_4$ or spirosiloxane $[2,4\text{-dimethylpentanedionato}]_2Si$.

Carbothermal feedstock preparation (for Path **2** processing). The Path 2 purified RHA was analyzed by TGA-DTA to determine the exact carbon, water and silica content. Depending on the initial RHA carbon content (2-20 wt. %) and the amount of silica extracted, the final RHA has a SiO_2:C molar ratio of 1:0.12-2.5. In practice, a 1:1.4 ratio is preferred as a small addition of graphite powder to the feedstock (as low as 1 wt. % of carbon in the feedstock) helps keep the electric arc amperage stable. The feedstock is formed as noted above.

Carbothermal reduction

The in-house built EAF used in these studies is shown in Figures **1** and **2**. A Goldstar 652 50 kW adjustable DC transformer (Miller electrics, Appleton, WI) is connected to the high purity graphite electrodes. The top electrode works as the anode and is lowered and raised by a linear actuator. The bottom electrode is actually the crucible used for the process. During the runs the operator manually dials the desired transformer amperage to keep the arc at ± 5%.

Voltage is dependent on the arc current, the distance between the top and bottom electrode, the temperature in the system and the amount of gaseous SiO produced in the system (higher concentration of SiO decrease the voltage). During the run, the operator remotely adjusts the top electrode up or down to keep the voltage constant (initially at 40-45 V, increased to 60-65V progressively over 1 h. An arc voltage of 60-65V provides the most stable arc once SiO forms in the system) to compensate for the change in concentration of SiO. The top electrode is progressively consumed during the run. As this system does not allow to pour the molten silicon, the silicon is collected after it has solidified: the crucible is shattered and the broken silicon (generally 2-5 cm pieces) collected as seen in Figure **7**.

Elemental analysis.

Trace impurities in the as-produced silicon were analyzed using an Ultima ICP-OES from Horiba Jobin-Yvon. The ICP-OES was calibrated before each set of analyses using NIST traceable standards purchased from Teledyne Leeman Labs (Hudson, NH). Note that the limit of detection of the ICP-OES used are in the 0.2 part per billion per weight range depending on the element, well below what is needed to detect the amount of impurities reported even in the diluted solutions.

Each analysis was run on 3 different samples from each batch and averaged to compensate for potential difference in impurities depending on location in the furnace (each sample itself being analyzed 3 times and averaged also) as we were not able to document differences between depths in the furnace due to our EAF design.

In addition while the furnace was in operation, the arc was momentarily turned off and a sample of the molten silicon was taken using high purity graphite tools and poured into a graphite crucible. The resulting 1 g sample of silicon was sent to the Evans analytical group (Sunnyvale, CA) and analyzed by glow discharge mass spectroscopy. Due the difficulty of obtaining this sample in our system and the high danger to the operator this experiment was not done on every batch.

Silicon Approximately 1 g of sample removed from the reactor was placed in 12 mL of trace grade hydrofluoric acid (37 wt. %, 20 ppmw fluorosilicic acid, all metal impurities ≤ 1 part per billion by weight) placed in a PTFE beaker cooled in an ice bath and 6 mL of trace grade nitric acid (37 wt. %, all metal impurities ≤ 1 part per billion by weight) was added dropwise and a PTFE cover placed on top. Once dissolution was complete, the solution was then filtered and diluted to 30 ML with electronic grade water.

RHA (0.5 g) samples were placed in a PTFE pressure vessel; 10 mL of trace grade HF (37 wt. %, 20 ppmw fluorosilicic acid, all metal impurities ≤ 1 part per billion by weight) was added, then 10 mL of aqua regia: 2.5 mL of trace grade HNO_3 (37 wt. %, all metal impurities ≤ 1 part per billion by weight) and 7.5 mL of trace grade HCl (37 wt. %, Br 10 ppmw, all metal impurities ≤ 1 part per billion by weight) The solutions were micro-waved for 15 min, cooled at -10°C overnight, this process was repeated four times. At this point the solutions were filtered, diluted to 40 mL with electronic grade water.

Transmission electron microscopy, elemental mapping A JEOL 3100R05 Double C_s-Corrected analytical electron microscope TEM/STEM was used for this analysis. A sample of purified RHA (as described in Path 1) was dusted on a TEM grid coated with a holey carbon film. Pictures were taken using high-angle annular dark-field imaging with the TEM in scanning transmission electron microscopy mode. Element mapping was done using X-ray Energy Dispersive Spectroscopy to show the distribution of C and Si.

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