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The Importance of New “Sand-to-Silicon” Processes for the Rapid Future Increase of Photovoltaics

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By the end of 2019, more than 0.5 terawatts (TW) peak power was converted cumulatively by all photovoltaics (PVs) installed on this planet, the largest value in recorded human history.[1] Simultaneously, the total global power consumption surpassed 18 TW,[2] also the largest ever value to date. Continued expansion of PVs at a sufficiently accelerated rate to bridge this supply/demand gap *in the near term* will be greatly facilitated by semiconductor materials suited for immediate mass production. In this context, “ideal” semiconductors are those that satisfy the following four criteria. First, the chemistry/physics/metallurgy of the material should be comprehensively understood so as to allow efficient device construction. Second, upon installation and regular operation, the semiconductor material should be practically indestructible, affording indefinite operation. Third, the semiconductor material should present no immediate or potential health hazard to the area in which it is housed. Fourth, the availability, collection, and manufacture of the semiconductor material should be uncomplicated, require minimal infrastructure, and present no long-term environmental consequences.

Although many semiconductor compounds show promise in one or more of these criteria,[3] crystalline silicon (Si) is arguably the only semiconductor to unambiguously satisfy at least three of these criteria. Si has been exhaustively studied since the advent of the modern semiconductor industry. Methods for doping, homojunction/heterojunction formation, and surface passivation are all known and significantly more advanced relative to almost every other material.[4,5] Accordingly, crystalline Si PVs exhibiting energy conversion efficiencies over 20% were first demonstrated more than **three decades** ago.[6] More specifically, Si is such a well-understood material that the remaining loss mechanisms in crystalline Si PVs are so sufficiently identified that devices with efficiencies that approach the thermodynamic Shockley−Queisser limit now exist.[6] Regarding longevity, few PV materials have been commercially available to the general public for an extended amount of time. More tacitly, commercial crystalline Si panels and modules have been available for residential power sources since the late 1970s/early 1980s and are presently sold with warranties lasting longer than **two decades**. Anecdotally, there are reports of residential Si PV installations that still function after **four decades** of operation with minimal or no maintenance.[7] Hence, while stability arguments can be made only by extrapolation for the majority of non-Si PVs, there is no ambiguity for Si PVs. On the matter of toxicity, crystalline Si presents no known bio- or environmental hazard and causes no adverse effects to human health. Even in the scenario where the Si module is catastrophically destroyed (e.g., burned in a fire), the release of crystalline Si poses no immediate or long-term environmental risk. For reference, zerovalent crystalline Si is sufficiently biocompatible that it is a key component in promising *in vivo* drug delivery therapies.[8]

Crystalline silicon is arguably the only semiconductor to unambiguously satisfy at least three of these criteria.

The *only* argument against crystalline Si as the ideal PV material both now and in the future pertains to the fourth criterion. That is, the availability, collection, and manufacture of crystalline Si are extremely problematic. More precisely, because Si in nature is found only as impure, oxidized sand (silica/SiO_2) or silicates (a salt with $SiO_{4-x}^{(4-2x)-}$), the chemistries required for purification, reduction, and crystallization are unavoidable. Unfortunately, the approaches used for these processes industrially are complex, costly, and polluting, manifesting in intolerably high fiscal and environmental costs for crystalline, solar-grade Si PVs. This point is expounded in the following section, but the bottom line is clear. The deficiencies in the existing chemistry used to

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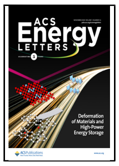

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transform raw "sand" to crystalline, solar-grade Si are the last major frontier for Si photovoltaics. Cutting the cord on the existing "sand-to-Si" chemistries and realizing new, more efficient and less intensive processes would facilitate continued and rapid proliferation of Si photovoltaics (Figure 1).

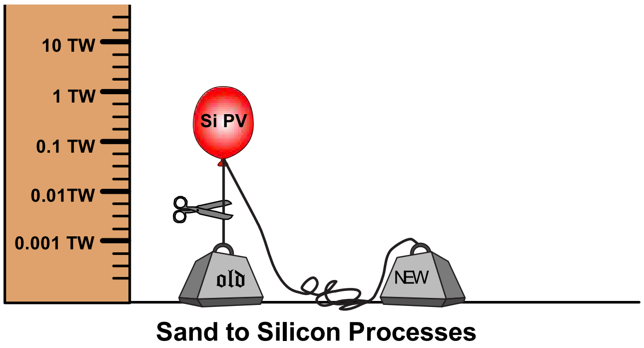

Figure 1.

The Status Quo: High-Temperature "Sand-to-Si" Processes. Figure 2 summarizes the existing "sand-to-Si" strategy employed by the current Si PV industry. The basic philosophy is to take feedstock SiO_2/silica and reduce it, then purify the resultant zerovalent solid, and finally recrystallize it into forms that can be further processed into devices.

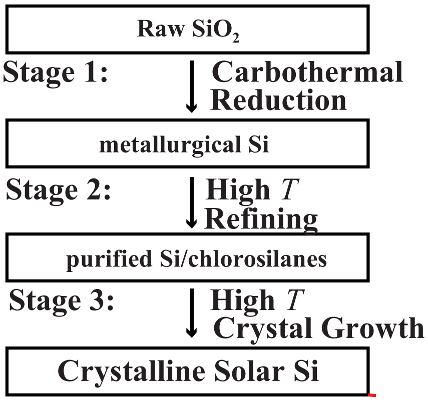

Figure 2. Graphical summary of the existing "sand-to-Si" approach used today in the crystalline Si PV industry.

Carbothermal reduction of SiO_2, a 19th century chemical innovation,[9] is overwhelmingly the dominant process for the first stage in the Si industry today. This reaction is performed with graphitic carbons as the reducing equivalents for converting lumpy quartz[10] to zerovalent Si within electric arc furnaces. Reaction 1 describes this reaction, typically performed at $T \geq 1900$ °C.[11]

$$SiO_2(s) + 2C(s) \rightarrow Si(l) + 2CO(g) \qquad (1)$$

Reaction 1 is deceptively brief, as it represents the net sum of multiple reaction steps with several intermediates that form and react in various reaction zones within the furnace.[10,12] The product of reaction 1, metallurgical Si, is not nearly pure enough (<99.9%)[5,13−16] for PV use. Although highly refined silica and clean carbon sources (e.g., pyrolytic graphite) have been previously explored to produce "cleaner" metallurgical Si,[10] the viability of reaction 1 is actually better *in the presence* of impurities. For example, the presence of Fe helps ensure that the thermodynamically favored product SiC reacts with gaseous intermediate SiO(g) to decompose quickly into Si and CO rather than accumulate.[12] Moreover, the presence of nonmetal impurities (e.g., B and P) in solid source quartz and carbon is almost unavoidable[17] because natural, high-purity quartz is scarce and only a few suppliers even sell rigorously purified silica/quartz.[10,18] Accordingly, the existing reduction chemistry in Si manufacturing produces low-purity Si that mandates extensive refining of the product.

The operation of arc furnaces for metallurgical-grade Si requires roughly 12 kWh kg^{-1} of electricity,[15,19] translating into an energy input of 1.2 MJ mol^{-1} Si. Significantly more energy is required for refining this Si.[14,15] The majority of refining methods for obtaining solar-grade crystalline Si involve first melting metallurgical Si (T_m = 1414 °C), then applying some chemical or physical process, followed by some form of controlled precipitation (e.g., directional solidification, crystal nucleation/growth)[10,13,16] to yield crystalline Si suitable for PV. Correspondingly, some combination of high temperatures, strongly oxidizing environments, caustic (strongly acidic or basic) conditions, and alloying reactions are necessary.[5,15] The approximate net energy requirement for refining metallurgical Si is 20 kWh kg^{-1} (2 MJ mol^{-1}). This energy input literally represents a substantial "entropic penalty" that is necessary to realize purified, solar-grade Si. Refining of metallurgical Si generates approximately 14 kg of waste per kg of solar-grade crystalline Si.[20] Alternatively, chemical purification (e.g., Siemens, Bayer, and fluidized bed reactor processes)[13,14,21] is possible if the solid metallurgical Si is first gasified into molecular silanes. This strategy has the advantage that silanes can be readily distilled, separated, and purified to a much greater degree than molten Si. The disadvantage of such chemical methods is that they generate **extremely** toxic intermediates/side products, involve corrosive reaction conditions (e.g., stoichiometric HCl and high pressures), and are also energy intensive (e.g., the Siemens process requires another 90−200 kWh kg^{-1} or 9−20 MJ mol^{-1} of Si).[5] With these methods, containment and waste-handling strategies are critical and add further infrastructure demands.

The Dollars and Cents of High-Temperature "Sand-to-Si" Processes. The fiscal cost of crystalline, solar-grade Si is a complex amalgamation of several related and unrelated factors, including geopolitical policies, resource availability, infrastructure requirements, and waste handling. In general, the fiscal cost of crystalline Si PVs has continuously decreased the last several decades,[5,13,14] due in part to innovations in production processes, lower Si loss during processing, and less consumption of Si in PV architectures.[5,6,14,22−25] However, the most substantial drops in the cost of crystalline Si that occurred within the past decade were fueled by foreign government subsidies. Specifically, China's deep commitment to augment their production capacity of crystalline Si flooded the market, making crystalline, solar-grade Si readily available and affordable for consumers.[26,27] This dramatic, recent drop in fiscal cost cannot be confused with the permanent price lowering that is necessary for Si PV to reach the 18+ TW scale. Specifically, the loss of these subsidies and/or a decreased commitment to further support the growth of the Si industry by China,[26] in addition to other international tariff policies or unforeseen geopolitical disasters,[28] would result in a rapid and significant threat to the continued and expanded manufacture of crystalline, solar-grade Si.

The fiscal costs of purifying and refining Si are directly reflected in two numbers. First, the change in price of Si from the raw feedstock to solar-grade material is substantial. The per mass value of sand (\$0.05 kg^{-1})[29] is more than 2 orders of magnitude lower than the corresponding price of crystalline, solar-grade Si. Presently, the value of crystalline, solar-grade Si ($\sim$\$10 kg^{-1})[30] reflects the strong market influence that foreign governments' subsidies and commitment to building the infrastructure for purifying, reducing, and crystallizing chemistries have had on the global price of Si.[31] Without that external factor, the price of crystalline, solar-grade Si would likely be higher ($\sim$\$70 kg^{-1}).[14,15] Second, the cost of setting up new manufacturing facilities of crystalline, solar-grade Si is significant. For reference, the last new facility built in the United States cost an estimated \$2.5 billion.[32] The fiscal cost of Si refining translates into extremely small profit margins, eliminating any incentive for new domestic manufacturers of crystalline, solar-grade Si.[13,23,25] Even existing stalwart Si companies like SunPower Corporation have abandoned their own Si manufacturing, choosing to outsource this work instead to foreign entities.[33]

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The Environmental Cost of High-Temperature "Sand-to-Si" Processes. Through decades of technical advances, the state-of-the-art practices in the industrial manufacture of crystalline, solar-grade Si recycle input materials and minimize waste accumulation.[20] Still, these engineering innovations do not change the underlying thermodynamics. The bond dissociation enthalpy of Si−O is 418 kJ mol^{-1} (100 kcal mol^{-1});[34] that is, scission of these bonds in a solid SiO_2 lattice is fundamentally energy intensive. When thermal energy alone is used to drive bond-breaking chemistry, the environmental consequences are severe. For example, the total electric power consumed just by heating during carbothermal reduction and refining is large and highly polluting. For reference, ~27 kg of carbon are consumed and ~84 kg of CO_2 are emitted for every 1 kg of polycrystalline Si.[20] The excessive temperatures required to process molten Si also exacerbate contamination. The removal of B and P impurities is particularly difficult, as the equilibrium partition coefficients for these elements is often very close to Si.[10,16] Overall, even with the best waste-handling strategies, the environmental impact of industrial Si refining performed at the large scale necessary for PVs is considerable when the input electrical power is supplied by fossil fuel sources.[20] These sum points are best encapsulated by the energy payback time of crystalline solar-grade Si, i.e., the time a PV takes to convert the equivalent energy used to complete "sand-to-Si" chemistry used in its manufacture. Even utilizing the most advanced photovoltaic cell designs, the energy payback times of crystalline solar-grade Si PVs are on the time scale of years.[35]

Alternative Low Temperature "Sand-to-Si" Processes. Avoiding carbothermal reduction inherently changes infrastructure requirements (e.g., electrical power consumption, heating apparatus, corrosion-resistant reactors, etc.) and widens the possibilities for purification strategies. That is, by avoiding metallurgical Si as an intermediate, a large entropic penalty can be mitigated. As demonstrated by the Siemens process, distillation of molecular forms of Si is potentially more effective than refining solid metallurgical Si. Doing so prior to the reduction step could eliminate the need/presence of hazardous byproducts. Figure 3 presents one hypothetical, alternative "sand-to-Si" scheme. The benefit of such a "sand-to-Si" route is realized only if the energy and infrastructure requirements are significantly lower than those used for carbothermal reduction, gas-phase refining, and melt crystal growth in Figure 2.

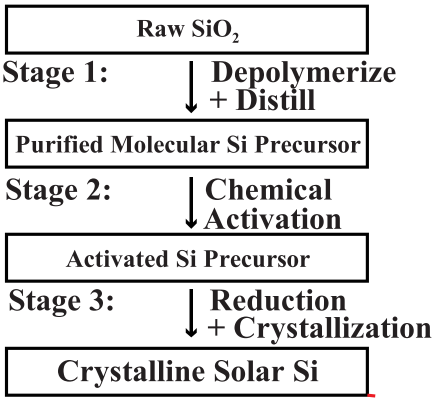

Figure 3. Graphical summary of an alternative "sand-to-Si" manufacturing/refining strategies where purification is the first stage and reduction is performed last.

Advances in Silica Purification. Several methods are known for purifying solid SiO_2/silica,[36−38] but none is simultaneously efficient, fast, and inexpensive. Case in point, purification of solid SiO_2/silica is sufficiently arduous and resource intensive that scarce, naturally low-impurity "white" sands are highly coveted.[39] One method for removing impurities from impure sands is through the dissolution of solid SiO_2/silica into molecular/ionic monomers, i.e., "SiO_2 depolymerization".[11,40] Driven by the interest in synthesizing Si-based commodity chemicals, numerous depolymerization reactions with organic alcohols that produce alkoxysilanes have been developed.[41,42] Historically, these reactions suffered from requiring stoichiometric amounts of base and low yields.[11] However, two recent advancements have dramatically improved the viability of this transformation. Reactions that produce spirocylic alkoxysilanes can be obtained by SiO_2 depolymerization using catalytic amounts of base.[11,40] Such alkoxysilanes are attractive because they can be readily distilled, facilitating purification. Similar depolymerization reactions have been recently shown with primary alcohols and substoichiometric amounts of base, facilitating the large-scale preparation of valuable tetraalkoxysilanes like tetramethoxysilane.[43] Recent computational results further suggest that depolymerizing solid SiO_2/silica reactions can even be exergonic with more strongly chelating alcohols (e.g., diols) at temperatures near the boiling point of water.[44]

Advances in Chemical Reductions to Produce Si. All known metallothermic reductions, i.e., reaction of SiO_2 at elevated temperature with metal reductants to produce zerovalent Si, require thermal activation. Among the pure metals, magnesiothermic and aluminothermic reductions occur at the lowest known temperatures of $T > 600$ °C and $T > 650$ °C, respectively.[45,46] A metallothermic reduction between activated silica and an alloy of Mg and Al was recently demonstrated at an unusually low temperature of $T = 450$ °C.[46] It is not clear if other alloy compositions could further lower the reaction temperature, the manner in which the metals catalyze the reaction, and the role that the properties of silica play. Ultimately, the method of producing the metal reductants themselves must also be considered, as they are typically obtained by electroreduction. Nevertheless, the advances in metallothermic reduction are encouraging.

Advances in Si Electrodeposition. Historically, Si electroreduction strategies have been sought because they (1) utilize the cleanest reductant imaginable, electrons; (2) can be natively simple in terms of required infrastructure; and (3) are easily scaled.[47,48] A ground-breaking report in the early 2000s demonstrated the direct electroreduction of solid SiO_2 by electrochemical "deoxygenation".[49] More recent advances have focused on Si electrodeposition using dissolved, activated forms of SiO_2. For example, molten salt electrolytes containing calcium oxide and calcium chloride have been shown to form active complexes with dissolved SiO_2 that facilitate electrodeposition of polycrystalline Si at $T = 850$ °C,[50] with sufficient purity for functional PV devices.[51,52] SiF_6^- has also been demonstrated as a potential oxidized precursor for crystalline Si electrodeposition in molten salts at similar temperatures.[53−55] A separate tactic utilizes chlorosilanes in conjunction with liquid metal electrodes in common solvents to electrodeposit crystalline Si at extraordinarily low temperatures,[56,57] with the possibility of growing single-crystalline, epitaxial thin films.[58] Whether individually or in combination, these innovations suggest there are new and fertile opportunities in Si electrodeposition.

Summary and Outlook. Si PVs make up approximately 90% of the total produced, installed, and operating solar cells on earth today.[15] The status quo methodology for manufacturing and refining crystalline solar-grade Si has been enormously successful in maturing Si PV technologies to this point. However, this is not enough. More than 1 order of magnitude more PVs are needed to meet all of society's current and future energy demands. Continued reliance on the current chemical strategies in Si manufacturing dramatically dims the prospects of sunlight as society's primary energy source in the near future. To realize the benefits of Si PV at the 18+ TW scale, a reimagining of how society produces crystalline Si PV is mandatory. New chemical approaches are needed to harness and utilize raw, impure, and imminently abundant silica feedstocks. Identifying simpler, more direct chemical and electrochemical SiO_2 reductions is arguably the most potent CO_2 remediation strategy. To this end, **now** is the time to realize new "sand-to-Si" processes that ensure the future of solar energy.

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Notes

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