Solar-Grade Silicon from Metallurgical-Grade Silicon Via Iodine Chemical Vapor Transport Purification

Preprint

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ABSTRACT

In an atmospheric-pressure “open” reactor, SiI₂ transfers from a hot (>1100°C) Si source to a cooler (>750°C) Si substrate and decomposes easily via 2SiI₂ → Si + SiI₄ with up to 5µm/min deposition rate. SiI₄ returns to cyclically transport more Si. When the source is metallurgical-grade Si, impurities can be effectively removed by three mechanisms: (1) differing free energies of formation in forming silicon and impurity iodides; (2) distillation; and (3) differing standard free energies of formation during deposition. Distillation has been previously reported. Here, we focused on mechanisms (1) and (3). We made feedstock, analyzed the impurity levels, grew Czochralski single crystals, and evaluated crystal and photovoltaic properties. Cell efficiencies of 9.5% were obtained. Incorporating distillation (step 2) should increase this to a viable level.

INTRODUCTION

A projection by one of the large polysilicon manufacturers indicates that PV demand for reject Si from the electronics industry will exceed the supply (8000 metric tons/yr) by a factor of 2 to 4 by the year 2010 [1]. Of the more than 300 MW of photovoltaic modules sold per year, about 85% are made from silicon. Si PV manufacturers have repeatedly expressed concern about the future supply of low-cost feedstock as this market continues to grow by more than 30%/year. The issue is to supply solar grade silicon (SoG-Si) feedstock with the necessary purity (~99.999%) at an acceptable cost. We report research on a new approach for producing SoG-Si from metallurgical-grade silicon (MG-Si) based on atmospheric pressure iodine vapor transport (APIVT).

ATMOSPHERIC PRESSURE IODINE VAPOR TRANSPORT PURIFICATION OF SILICON

Our work on the growth of thin-layer Si at atmospheric pressure by APIVT [2] led us to explore its applicability to MG-Si purification. Iodine reacts with Si to form SiI₂, which reacts further with silicon at high temperatures to form SiI₄. SiI₂ decomposes easily with a silicon deposition rate >5µm/min when the source Si temperature is ~1200°C and the substrate temperature is approximately 1000°C. When MG-Si is used as the source material, impurities can be effectively removed in several ways:

(1) During the initial reaction between iodine and MG-Si, the formation of impurity iodides will be advanced or retarded (relative to the formation of SiI₂) depending on their free energies of formation. (2) Purification of SiI₄ by distillation in a cyclic process will cause metal iodides with vapor pressure lower than that of SiI₄ to remain at the bottom of a distillation tower, and those with higher vapor pressure to rise to the top. For example, at one atmosphere, carbon tetra iodide boils at 19°C higher than SiI₄ and phosphorous tri-iodide at 63°C lower. These large differences permit easy separations. (3) During the deposition of silicon from SiI₂, most metal iodides have a large negative value of standard free energy of formation, so they are more stable than SiI₂ and SiI₄. These iodides will form readily in the gas phase, but have only a small tendency to be reduced again in the deposition zone. An example of this behavior is AlI₃ [3]. The cyclic APIVT refinement process incorporating all three of these components [4] is shown in Fig. 1.

In Fig. 1, MG-Si and I are introduced into a crucible or liner at the bottom of a cold wall reactor and heated to temperature T₁. At first, T₁ is ~500°C–1000°C. Silicon and some impurities react with iodine to form SiI₄ and impurity...
iodides. Some tri-iodides of B and P are removed from the distillation plate near the reactor top (T ≈ 120°C). The purer gases condense on the wall of the reactor and flow into the distillation tower that is heated at the bottom to T3 ≈ 310°C. With most metal iodides retained in the liquid, Cl4 vaporizes and condenses on the lower and hotter distillation plate (T6 ≈ 205°C) whereas BI3 and PI3 are collected at the highest and coolest plate (T5 ≈ 120°C). The purified SiI4 is collected at the middle plate (T4 ≈ 185°C) and returns to the crucible/liner at the reactor bottom. After this initial start-up, the temperature in the crucible is turned up to T1>1000°C. The purified SiI4 further reacts with Si at this temperature to form SiI2, which transports from hot regions to cooler ones. SiI2 is very unstable and easily decomposes into Si and SiI4 at the provided substrate surfaces (high-purity silicon slim rods, tubes, etc.) heated to T2>750°C. The recycling SiI4 (together with additional impurity iodides) goes through the distillation process again before returning to the reactor bottom.

As MG-Si is consumed, it is replenished through a gas-purged feed port. This gas purge is above an equilibrium iodine and iodide cloud layer that forms at a height corresponding to an appropriate temperature region cooler than T2. A similar purge above the cloud in the main reactor can allow removal of deposited purified silicon, thus affording a continuous process at approximately atmospheric pressure. Volatile gases are kept in the system by the cloud layer due to condensation and gravity effects described in [2]. The entire reactor wall within the dotted frame must be kept "cold" at between 120° - 700°C to prevent silicon deposition on the walls.

SiI4 distillation [step (2) above] has been previously studied [5,6], so we focused on investigating purification by the initial reaction between iodine and MG-Si and by the final deposition of silicon from SiI2 [steps (1) and (3) above]. First we grew ~100-µm-thick epitaxial layers of Si by APIVT from a MG-Si source onto high-purity, single-crystal substrates. Impurity levels in these layers are shown in Fig. 2. They were analyzed by secondary ion mass spectroscopy (SIMS) and glow discharge mass spectroscopy (GDMS). Also shown are the MG-Si source material impurity levels determined by GDMS. The vertical lines show the permissible range of impurities in SoG-Si, dependent on growth method, with the upper limit for slow directional solidification and near equilibrium segregation, whereas the lower limit is for growth with little or no effective segregation, such as is the case for some ribbon growth processes. The selective APIVT pick-up, transport, and deposition of silicon reduced the concentration of all major impurities by more than several orders of magnitude, except for B (and P, not shown). Addition of the distillation step (2) should reduce B and P to the SoG-Si specification.

CRystal Growth and Analysis

Multiple large-area substrates in the form of concentric quartz cylinders were used for APIVT growth of thick layers from a MG-Si source. These layers were harvested and melted as feedstock for Czochralski (CZ) crystal growth and analysis. Figure 3 is a picture of a small <100> CZ single crystal grown from this material. The melt was clean, and no unusual problems were observed in growing crystals from the APIVT purified MG-Si feedstock. Table I shows the GDMS analysis of impurities in the MG-Si source and in the CZ crystal grown from APIVT-purified silicon. All metallic impurities are below the detection limits of the GDMS technique (values preceded by <), which, in the worst case, was 0.005 ppma. The predominant non-metallic impurities were O (17.6 ppma), C (14.3 ppm), P (6.8 ppm), and B (4.2 ppm). Thus, the crystal was highly compensated and mostly n-type, with $\rho = 0.3 \, \Omega \cdot cm$ near the tail end. However, a small region of the seed end was p-type with a resistivity of 0.4 $\Omega \cdot cm$. Diagnostic solar cells 2-mm x 2-mm in size were fabricated using a seed end wafer; they had an efficiency of 9.5%, as shown in Fig. 4, compared to an electronic-grade CZ-grown control cell efficiency of 13.8%.

![Fig. 2. Impurity contents in the MG-Si source material and in an epitaxial silicon layer grown by APIVT](image-url)
The cell parameter comparison between the CZ crystal grown from APIVT-purified feedstock silicon and the control CZ wafer grown from electronic-grade silicon is given in Table 2, and internal quantum efficiency is shown in Fig. 5.

Table 2. Cell Parameters for CZ Grown from APIVT-Purified Silicon and a Control CZ Wafer.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CZ control</th>
<th>CZ from APIVT Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Efficiency</td>
<td>13.8</td>
<td>9.5</td>
</tr>
<tr>
<td>( V_{oc} ) (Volts)</td>
<td>0.59</td>
<td>0.57</td>
</tr>
<tr>
<td>( J_{sc} ) (mA/cm(^2))</td>
<td>29.9</td>
<td>21.6</td>
</tr>
<tr>
<td>Fill Factor (%)</td>
<td>78.4</td>
<td>77.0</td>
</tr>
</tbody>
</table>

From internal quantum efficiency and reflectance data for a cell made from CZ grown using APIVT feedstock, we deduced a diffusion length of 8 µm. The high degree of compensation and high levels of B and P likely influence the properties of the material. Incorporating the distillation step [step (2)] will probably be necessary to obtain better performance from the APIVT-purified feedstock.

**SUMMARY AND DISCUSSION**

APIVT MG-Si purification is attractive because of its fast deposition rates and atmospheric-pressure operation. The later provides the potential for continuous operation with relatively easy input of source material and withdrawal of product. We demonstrated reduction of metallic impurities by several orders of magnitude using steps (1) and (3) of this process. We were able to grow small CZ crystals from the limited amount of Si produced in our lab-scale APIVT reactor. The resistivity was \(~0.4\ \Omega\cdot\text{cm}, but
Compensated with both B and P present in relatively large quantities. This resulted in a relatively low solar cell efficiency of 9.5% and low diffusion length of 8 \( \mu \text{m} \). The carbon levels in the material are also higher than desired for reliable single crystal growth on a large scale.

Coupled with previously studied SiI\(_4\) distillation (step (2)) to remove B, P, and C, APIVT MG-Si purification could become a practical and economical method for manufacturing SoG-Si feedstock. Earlier work in the silicon/iodine system by C.S. Herrick [6] and G.H. Moates [5] used iodine to purify silicon in the sequential steps: Si + I \( \rightarrow \) SiI\(_4\) \( \rightarrow \) purified SiI\(_4\) (by e.g. distillation, solution recrystallization, or zone-refining/sublimation) \( \rightarrow \) thermo-decomposition of SiI\(_4\) into Si under a low pressure of \( \sim 3 \text{ mm Hg} \). Such a process is inherently slow and uneconomical, because SiI\(_4\) can only be decomposed in low pressure, and requires a vacuum system. A key advance is provided by our approach that utilizes the disproportionation reaction: Si + purified SiI\(_4\) \( \rightarrow \) SiI\(_2\) + purified SiI\(_4\) + purified Si, to deposit silicon at atmospheric pressure, similar to the operating principles in our previous thin-layer silicon growth [2], but with the addition of built-in SiI\(_4\) purification steps.

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REFERENCES


# Solar-Grade Silicon from Metallurgical-Grade Silicon Via Iodine Chemical Vapor Transport Purification: Preprint

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**Authors:** T.F. Ciszek, T.H. Wang, M.R. Page, R.E. Bauer, and M.D. Landry

**Abstract:**
This conference paper describes the atmospheric-pressure in an "open" reactor, SiI₂ transfers from a hot (>1100 °C) Si source to a cooler (>750 °C) Si substrate and decomposes easily via 2SiI₂ → Si + SiI₄ with up to 5 m/min deposition rate. SiI₄ returns to cyclically transport more Si. When the source is metallurgical-grade Si, impurities can be effectively removed by three mechanisms: (1) differing free energies of formation in forming silicon and impurity iodides; (2) distillation; and (3) differing standard free energies of formation during deposition. Distillation has been previously reported. Here, we focused on mechanisms (1) and (3). We made feedstock, analyzed the impurity levels, grew Czochralski single crystals, and evaluated crystal and photovoltaic properties. Cell efficiencies of 9.5% were obtained. Incorporating distillation (step 2) should increase this to a viable level.

**Keywords:** PV; atmospheric-pressure; solar grade silicon; chemical vapor transport purification; thin-layer Si; crystal growth; impurities; quantum efficiency; SoG-Si feedstock; refining/sublimation; thermo-decomposition;