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SOLAR-GRADE SILICON FROM METALLURGICAL-GRADE SILICON VIA IODINE CHEMICAL VAPOR TRANSPORT PURIFICATION

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ABSTRACT

In an atmospheric-pressure "open" reactor, SiI_2 transfers from a hot (>1100°C) Si source to a cooler (>750°C) Si substrate and decomposes easily via $2SiI_2 \rightarrow Si + SiI_4$ with up to 5µm/min deposition rate. SiI_4 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 TRANPORT 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 SiI_4, which reacts further with silicon at high temperatures to form SiI_2. SiI_2 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 SiI_2) depending on their free energies of formation. (2) Purification of SiI_4 by distillation in a cyclic process will cause metal iodides with vapor pressure lower than that of SiI_4 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 SiI_4 and phosphorous tri-iodide at 63°C lower. These large differences permit easy separations. (3) During the deposition of silicon from SiI_2, most metal iodides have a large negative value of standard free energy of formation, so they are more stable than SiI_2 and SiI_4. 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 AlI_3 [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°–1000°C. Silicon and some impurities react with iodine to form SiI_4 and impurity

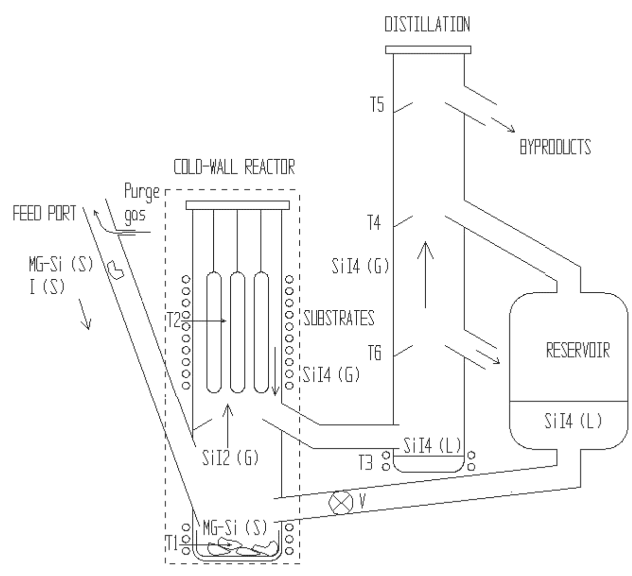

Fig. 1. Schematic of the cyclic APIVT MG-Si purification process incorporating components (1), (2), and (3)

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, CI_4 vaporizes and condenses on the lower and hotter distillation plate (T6 ≈ 205°C) whereas BI_3 and PI_3 are collected at the highest and coolest plate (T5 ≈ 120°C). The purified SiI_4 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 SiI_4 further reacts with Si at this temperature to form SiI_2, which transports from hot regions to cooler ones. SiI_2 is very unstable and easily decomposes into Si and SiI_4 at the provided substrate surfaces (high-purity silicon slim rods, tubes, etc.) heated to T2>750°C. The recycling SiI_4 (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.

SiI_4 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 SiI_2 [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 (14.3ppma), P (6.8 ppma), and B (4.2 ppma). Thus, the crystal was highly compensated and mostly n-type, with ρ = 0.3 Ω-cm near the tail end. However, a small region of the seed end was p-type with a resistivity of 0.4 Ω-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%.

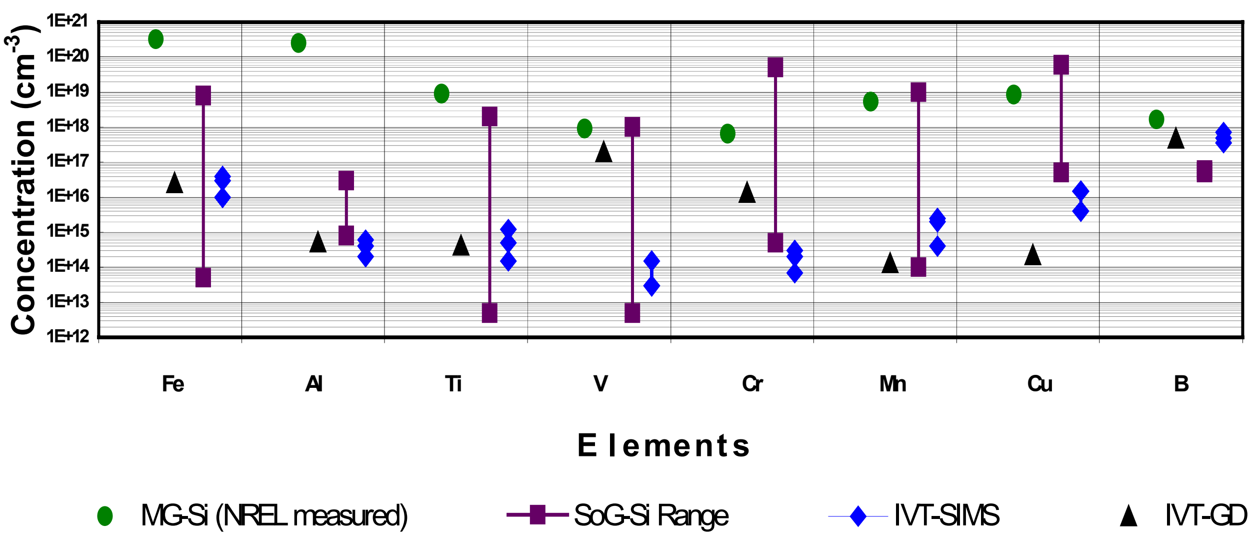

Fig. 2. Impurity contents in the MG-Si source material and in an epitaxial silicon layer grown by APIVT

Fig. 3. A 14-mm-dia. <100> CZ crystal grown from APIVT-purified MG-Si

Table I. GDMS Analysis of Impurities in MG-Si and in a CZ Crystal Grown from APIVT-Purified MG-Si (without SiI_4 distillation)

Element	CZ-Si from APIVT-Si [ppma]	MG-Si source [ppma]
B	4.157	14.548
C	14.264	107.565
O	17.554	66.706
Mg	<0.001	8.204
Al	<0.005	520.458
Si	Matrix	Matrix
P	6.801	21.762
S	<0.044	0.096
K	<0.007	<0.036
Ca	<0.007	44.849
Ti	<0.001	47.526
V	<0.001	143.345
Cr	<0.001	19.985
Mn	<0.001	19.938
Fe	<0.005	553.211
Co	<0.002	0.763
Ni	<0.002	22.012
Cu	<0.001	1.724
Zn	<0.002	0.077
As	<0.002	0.007
Sr	<0.0003	0.353
Zr	<0.0003	2.063
Mo	<0.001	0.790
I	<0.0002	<0.001
Ba	<0.0002	0.266
W	<0.0003	0.024

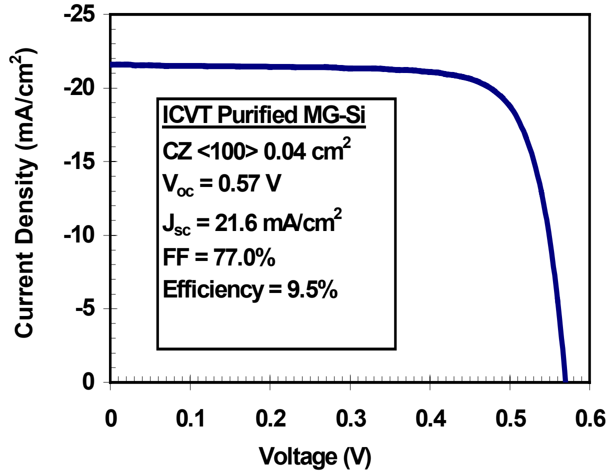

Fig. 4. Diagnostic solar cell parameters for a wafer from a <100> CZ crystal grown using APIVT-purified MG-Si

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.

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

From internal quantum efficiency and reflectance data for a cell made from CZ grown using APIVT feed-stock, 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 feed-stock.

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 with-drawal 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 Ω-cm, but

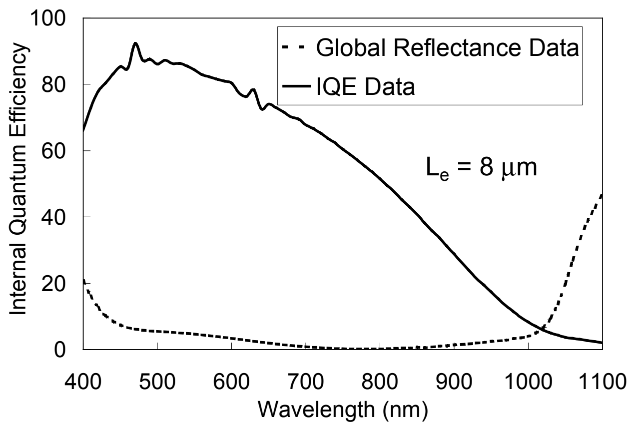

Fig. 5. Internal quantum efficiency (%) and reflectance (%) vs. wavelength

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 μm. 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 > SiI_4 > purified SiI_4 (by e.g. distillation, solution recrystallization, or zone-refining/sublimation) > thermo-decomposition of SiI_4 into Si under a low pressure of ~3 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 > 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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13. ABSTRACT *(Maximum 200 words):* This conference paper describes the atmospheric-pressure in an “open” reactor, SiI_2 transfers from a hot (>1100°C) Si source to a cooler (>750°C) Si substrate and decomposes easily via $2SiI_2 \rightarrow Si + SiI_4$ with up to 5□m/min deposition rate. SiI_4 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.

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