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Alternative Solar-Grade Silicon Feedstock Approaches

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ABSTRACT

Demand for reject electronics-grade silicon (EG-Si) feedstock will exceed the supply (8,000 metric tons/yr) by a factor of 2 to 4 by the year 2010. The photovoltaics industry would benefit from a low-cost supply of supplemental feedstock. We report research on four alternative methods for purification of metallurgical-grade silicon (MG-Si) to target levels suitable for solar-grade silicon (SoG-Si) use: (1) repetitive porous MG-Si etching, gettering, and surface-removal of impurities; (2) MG-Si gaseous melt treatment; (3) MG-Si purification by recrystallization of Si from MG-Si/metal solutions; and (4) iodine chemical vapor transport purification of MG-Si. Process descriptions and crystal growth and device results are presented.

1. Introduction

Eighty-seven percent of the more than 300 MW of photovoltaic (PV) modules sold per year are made from crystalline silicon. About 30,000 metric tons of solar-grade Si feedstock will be needed by the year 2010 [1], if the market continues to grow at 30%/year. We report research on four novel methods (listed in the abstract) for purification of low-cost, metallurgical-grade silicon (MG-Si).

2. Porous Etch Gettering/Removal of MG-Si Impurities

A treatment cycle started with porous Si etching, which creates preferential sites for impurity gettering, at room temperature using HNO₃/HF (1/100) for 6 min. Second, to facilitate diffusion of impurities to energetically favorable sites at surface, annealing was carried out for 30 min at 950°C in an argon ambient. Third, the porous Si surface layer containing accumulated impurities was converted to SiO₂ by oxidation at 950°C using an O₂ ambient and a prescribed cooling profile. Finally, the impurity-containing oxide layer was removed by a 10% HF solution dip for 10 min. We repeated the treatment cycle up to five times. By analyzing SIMS impurity profile data, we could project the number of cycles that would be necessary to meet the minimum purity requirements for SoG-Si. From 800 to more than 10,000 cycles would be required for bulk purification as shown in Table I – unrealistic in practice.

Table I. Impurity Area Density for Al, Cu, and Fe

Cycle #	Area Density (cm ⁻²)		
	Al	Cu	Fe
1	6.18x10 ¹³	1.68x10 ¹³	6.54x10 ¹²
2	8.44x10 ¹⁵	6.77x10 ¹²	1.85x10 ¹⁴
5	1.76x10 ¹⁴	9.16x10 ¹²	1.74x10 ¹⁴
Bulk (100μm)	2.50x10 ¹⁸	8.00x10 ¹⁶	3.00x10 ¹⁸
Cycles Needed	865	229,000	20,5000

3. MG-Si Gaseous Melt Treatment

We focused on boron removal from high-purity silicon melts doped with 20 ppm or 2x10¹⁸ atoms·cm⁻³ B. In separate experiments, four different gases [argon (Ar) for a control, Ar bubbled through distilled water, Ar bubbled through 37% ammonia solution, and ultra-high purity N₂] were introduced at about 1.5 liter/min through a quartz tube placed 2 mm above the melt for a treatment time of 2 h. The melts were then directionally solidified at a cooling rate of 1° C/min in a temperature gradient. Resistivity was used to determine resultant B concentration. Table 2 summarizes the resistivity measurements for each test. The most effective melt treatment was moist Ar. There was a 40% reduction of boron for a 2-h run. More B reduction is necessary for MG-Si purification, which could be achieved by processing the melt for longer times and bubbling the gas through the melt instead of directing it at the surface to improve the purification efficiency.

Table II. Boron Concentration After Gaseous Melt Treatment

Treatment	B (cm ⁻³)
Dry argon (control)	2.10x10 ¹⁸
Argon bubbled through 37% ammonia solution	1.35x10 ¹⁸
Dry nitrogen	1.30x10 ¹⁸
Argon bubbled through distilled H ₂ O	8.00x10 ¹⁷

4. Recrystallization of Si from MG-Si/Metal Solutions

If we use metals as solvents to dissolve MG-Si, recrystallization takes place at a much lower temperature than the 1412°C Si melting point. Most impurities exhibit retrograde solubility in silicon with peaks around 1300°C. Some of the most harmful elements in metallurgical-grade silicon, such as Ni, Co, Fe, and Cr, have their solubility in silicon decreased by more than one order of magnitude (from that at the silicon melting point) if the crystallization is done at temperatures below ~800°C.

An example of this eutectic recrystallization approach is the segregation coefficient k_{Al} of Al during Si recrystallization from a Al-Cu-Si ternary solution, based on the regular solution model:

$$k_{Al} = \frac{x_{Al}^s}{x_{Al}^l} = \frac{\gamma_{Al}^l}{\gamma_{Al}^s} \quad (1)$$

$$\gamma_{Al}^l = \exp \left[\frac{\Omega_{SiAl}^l (x_{Si}^l)^2 + \Omega_{AlCu}^l (x_{Cu}^l)^2 + (\Omega_{SiAl}^l + \Omega_{AlCu}^l - \Omega_{SiCu}^l) x_{Si}^l x_{Cu}^l}{RT_e} \right] \quad (2)$$

so

$$k_{Al} = \frac{\exp \left[2.43 (x_{Si}^l)^2 - 0.103 (x_{Cu}^l)^2 - 0.142 x_{Si}^l x_{Cu}^l \right]}{8991} \quad (3)$$

where x represents mole fractions, γ the activity coefficients, Ω the interaction parameters, R the Rydberg constant, and T the temperature.

Because both Ω_{SiAl}^1 and Ω_{SiCu}^1 are large positive numbers, Si-Al and Si-Cu interactions are repulsive in nature. Ω_{AlCu}^1 is negative, implying an attractive interaction between Al and Cu. Therefore, Cu in the growth solution will not only dilute Al, but will also retain Al in the liquid. A similar coupled analytical/experimental approach is under way for other silicon/metal solvent combinations.

5. Iodine Chemical Vapor Transport Purification

From our work on growth of thin-layer Si at atmospheric pressure [2], we know that iodine reacts with Si to form SiI_4 , which reacts further with silicon to form SiI_2 . SiI_2 decomposes easily at high temperatures, with a silicon deposition rate $>5\mu\text{m}/\text{min}$ when the source Si temperature is $>1200^\circ\text{C}$ and the substrate temperature is 1000°C . With MG-Si as the source material, impurities may be effectively removed in several ways: (1) differing free energies of formation; (2) distillation (e.g., at one atmosphere, carbon tetraiodide boils at 19°C higher than SiI_4 and phosphorous triiodide at 63°C lower); and (3) differing standard free energies of formation, affecting the tendency for reduction in the deposition zone. Distillation has been reported in earlier literature, so we focused on steps (1) and (3).

Large-area substrates were used for iodine chemical vapor transport (ICVT) growth of thick Si layers from a MG-Si source. The Si was harvested and melted as feedstock for Czochralski (CZ) crystal growth and analysis. Table III shows the impurity levels in the MG-Si source and in the CZ crystal grown from ICVT-purified silicon. All metal impurities are below detection limits and most other major impurities are significantly reduced, except for B, C, O, and P. Addition of the distillation step (2) should reduce B, C, and P to the SoG-Si specification. The crystal was highly compensated, with $\rho = 0.4 \Omega\text{-cm}$, p-type, near the seed end and $0.3 \Omega\text{-cm}$, n-type, near the tail end. Diagnostic solar cells from seed-end wafers had an efficiency of 9.5%.

6. Summary and Discussion

Of the novel MG-Si purification methods we presented here, ICVT is particularly attractive because it offers fast deposition rates and atmospheric-pressure operation. We demonstrated effective reduction of metallic impurities by several orders of magnitude. Coupled with SiI_4 distillation [step (2) mentioned above] to remove B, P, and C, this could lead to a very practical and economical method for manufacturing SoG-Si feedstock. Unlike the current silicon chlorosilane process for silicon feedstock, SiI_4 distillation is much less complicated and has no $\text{SiH}_n\text{Cl}_{4-n}$ intermediate compounds. Unlike the earlier SiI_4 -only based process that requires a vacuum system, our atmospheric pressure ICVT method is much faster and more convenient. A patent application is in process based on this work [3].

Porous-Si etch/gettering removal of impurities, although effective in the near-surface region, appears to be impractical for bulk purification because of the large

Table III. Analysis of Impurities in MG-Si Arc Furnace Material and in a CZ Crystal Grown from ICVT-Purified MG-Si (without the SiI_4 distillation step)

Element	CZ-Si from ICVT [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

< implies a level below the indicated detection limit.

number of process cycles that would be required. We have laid the modeling groundwork for MG-Si purification via recrystallization of Si from MG-Si/metal solutions, and have done a few experimental tests that show promise. However, considerable experimental work remains before a thorough assessment of this approach can be made.

Gaseous melt treatment with moist argon showed promise for reducing boron levels, but would require longer treatment times (~11 h) or more efficient exposure to the liquid silicon than we used in our lab experiments. We grew crystals and conducted analysis using a new type of SoG-Si feedstock developed by Crystal Systems. It is obtained by gaseous and slagging treatments of melted, heavily boron-doped (~200ppma) reject EG-Si from the electronics industry. The PV conversion efficiencies of 1-cm^2 devices made from CZ crystals we grew using the new treated hi-B EG-Si reject feedstock (14.0%, AR-coated) were up to 99% as high as those from CZ crystals we grew using EG feedstock.

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