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Float-Zone and Czochralski Crystal Growth and Diagnostic Solar Cell Evaluation of a New Solar-Grade Feedstock Source

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FLOAT-ZONE AND CZOCHRALSKI CRYSTAL GROWTH AND DIAGNOSTIC SOLAR CELL EVALUATION OF A NEW SOLAR-GRADE FEEDSTOCK SOURCE

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ABSTRACT

Czochralski (CZ) and float-zone (FZ) crystals were grown from experimental solar-grade silicon (SOG-Si) feedstock materials developed by Crystal Systems. The materials were metallurgical-grade Si and highly boron-doped p-type electronic-grade Si (EG-Si) reject material, both of which were gaseous melt-treated to remove boron. Crystal growth observations, lifetime and impurity characterization of the grown crystals, and device performance of wafers from them are presented. Devices made directly on treated high-B EG-Si feedstock have a little over half the efficiency of devices made from control CZ samples. However, devices on CZ and FZ crystals grown from the treated high-B EG-Si feedstock have comparable PV performance (14.0% and 13.8% efficiency, respectively) to that of CZ control samples (14.1%).

INTRODUCTION

A solar-grade silicon (SoG-Si) feedstock formation method under investigation by Crystal Systems (Salem, MA) treats molten metallurgical-grade silicon (MG-Si) with a sequence of gaseous and slagging processes to reduce impurities. The method has been particularly successful with boron impurity removal [1], although residual levels of phosphorous are higher than desired so far. The success with boron removal, historically considered to be one of the most difficult impurities to remove from silicon because of its low volatility and low segregation coefficient, could open the way to interim utilization of a heretofore unusable segment of the scrap electronic-grade silicon (EG-Si) supply. This is heavily boron-doped single-crystal, wafer, and epitaxial-wafer reject material. We grew Czochralski (CZ) and float-zone (FZ) crystals using Crystal Systems-treated MG-Si and particularly their treated highly boron-doped p-type EG-Si reject material as the feedstock. Observations on crystal growth, characterization of the grown crystals, and device performance of wafers from them are presented.

FEEDSTOCK MATERIAL

Working under a DOE-NREL PVMaT subcontract, Crystal Systems developed gaseous and slagging melt treatments focused toward an eventual cost-effective process for making SoG-Si feedstock from MG-Si. In using these treatment sequences on MG-Si, boron levels could be reduced from 20–60 ppma to ~0.3 ppma (1 Ω-cm), but phosphorous and carbon removal remain a problem. The treatment process was recently applied to highly boron-doped EG-Si scrap (boron content of 50–400 ppma). The available amount of this material is estimated to be equivalent to 100–200 MW/year. The Crystal Systems process reduces its boron content by several orders of magnitude, to approximately 1 ppma (0.4 Ω-cm, or 5 x 10^{16} cm^{-3}). Batch sizes of 60 to 140 kg have been treated. Although an integrated treatment procedure might process liquid silicon directly as it is tapped from the arc furnace in a MG-Si plant, followed by in situ slow directional solidification of a multicrystalline ingot for wafering into cell blanks, the smaller-scale initial experiments considered only the melt treatment step. Solid MG-Si or boron- doped reject EG-Si was loaded into a crucible and melted, treated, and solidified, but the directional solidification was sub optimal for direct ingot use because a dual-use furnace with proper features for both treatment and directional solidification has not yet been implemented. The solidified, treated silicon was core drilled to form feed rods for FZ growth and crucible charges for CZ growth. The shaped pieces were degreased and etched in 3:1:2 mixed acid prior to crystal growth. The treated high-B EG-Si and MG-Si feedstock are both dense and remain intact through shaping, cleaning, and etching steps. They are also suitable as substrates for epitaxial growth.

FLOAT-ZONE AND CZOCHRALSKI CRYSTAL GROWTH

Float-zone growth

FZ growth was carried out on treated high-boron content scrap EG-Si using RF heating with a stationary one-turn coil operating at 2 MHz in an argon ambient at 0.3 bar above atmospheric pressure, to minimize heater or crucible sources of O, C, and other impurities. The feedstock diameter was about 27 mm, and crystals of this diameter or somewhat larger were grown. The typical growth rate was 3 mm/min with a 13–16 rpm crystal rotation rate and a 2–3 rpm feed rod rotation rate (crystal on the bottom, moving downward). A clean initial melt allowed good seed contact and initiation of dislocation-free (DF) growth. No gas evolution or cracking of the feed-

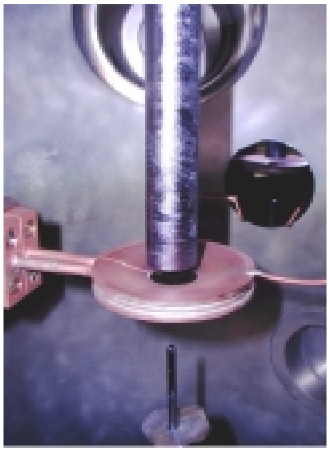

Fig. 1a. FZ set-up

Fig. 1b. FZ growth

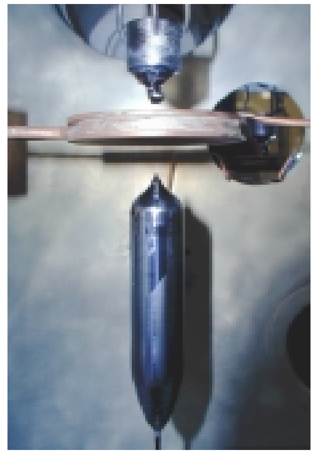

Fig. 1c. Finished FZ ingot

Fig. 1d. Frozen particulates

stock occurred during the growth process. DF growth was maintained for about half the ingot length, then twins and later, grain boundaries formed. Figure 1 illustrates the set-up, growth, and finished ingot. Late in the growth process, floating clumps of particulates could be observed on the melt, and these grew in size and froze onto the ingot surface during the crystal termination (Fig. 1d). A similar particulate formation situation was seen using treated MG-Si feedstock, but was generally more severe, with DF growth terminating earlier and more massive particle clumps on the melt and freeze-out.

Czochralski growth

As for FZ growth, CZ growth from treated, high B-content, reject EG-Si material was characterized by a clean initial melt that allowed seeding and necking to initiate DF growth. The ambient was argon at 0.1 bar above atmospheric pressure. Induction heating at 0.4 MHz melted the Si held in a stationary clear fused quartz crucible nested in a graphite susceptor. The growth rate was 1.5 mm/min with a crystal rotation rate of 14 rpm. One small CZ crystal grown from the treated high-B EG-Si feedstock remained DF throughout its length. Two others initiated twins and later grain boundaries after roughly half of the melt was solidified. Clumps of particles could be seen on the frozen melt residue from these runs, similar to those observed in FZ growth. Figure 2 shows the set-up, CZ growth, a finished CZ ingot, and an example of the particle clumps on a frozen melt residue surface. No CZ growth was attempted using treated MG-Si feedstock.

FZ AND CZ CRYSTAL CHARACTERIZATION AND DIAGNOSTIC PV DEVICE RESULTS

A Nomarski photomicrograph of a frozen particle clump that formed on the surface of a FZ crystal grown from treated MG-Si is shown in Fig. 3. The hexagonal morphology of the particles, coupled with electron probe micrograph analysis (EPMA) detection of high levels of C, provides at least circumstantial evidence for SiC particle composition—likely forming by precipitation from saturated carbon solubility levels in the melt.

Bulk determinations of C and O content in treated high-B EG-Si feedstock, CZ and FZ ingots grown from it, and a CZ ingot grown from EG-Si control feedstock (doped to 0.7 Ω-cm p-type) were made by Fourier transform infrared spectroscopy (FTIR). In Table I, higher levels of C are seen in the treated EG-Si and the CZ crystal grown from it than in the CZ crystal grown from high-purity EG-Si. O levels are comparable. Table 2 gives the measured impurity levels, by glow-discharge mass spectroscopy (GDMS), for the melt-treated high-B EG-Si feedstock, and for both CZ and FZ crystals grown

Fig. 2a. CZ set-up

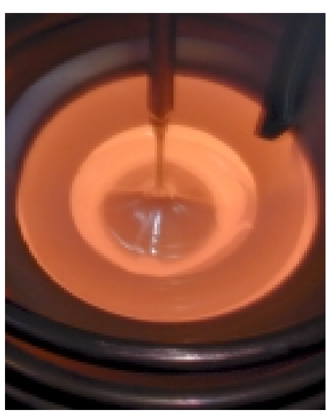

Fig. 2b. <100> DF CZ growth

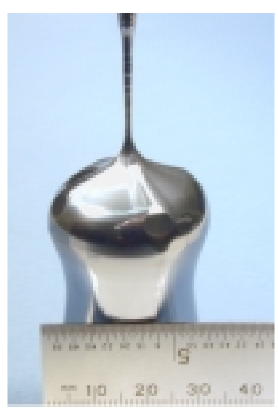

Fig. 2c. <100> CZ ingot

Fig. 2d. Particulate clumps

Table I. Properties and Diagnostic Solar Cell Performance of Treated, High-B Reject EG-Si Feedstock, CZ and FZ Crystals Grown from It, and a CZ Control Crystal Grown from Doped EG-Si Feedstock.

Sample	Source	C (cm^{-3})	O (cm^{-3})	ρ (Ω-cm)	Lifetime (μs)	Cell Efficiency with ARC* (%)
3-28M5D	Treated hi-B EG-Si feedstock	$4x10^{17}$	$6x10^{17}$	0.4	0.3 - 0.9	8.3
CZ-010309	CZ from treated hi-B EG-Si feedstock	$1x10^{17}$	$1x10^{18}$	0.4	7 - 10	14.0
FZ-010222	FZ from treated hi-B EG-Si feedstock	$4x10^{17}$	$<1x10^{17}$	0.4	130	13.8
CZ-010302	Control CZ from EG-Si feedstock	$5x10^{16}$	$1x10^{18}$	0.7	15 - 22	14.1

*ARC – Antireflection Coating

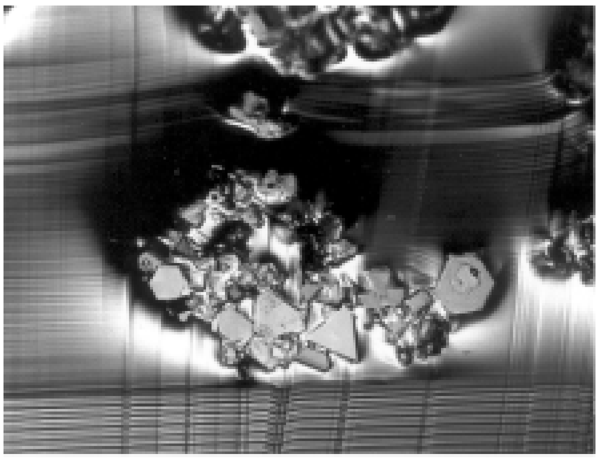

Fig. 3. Optical photomicrograph of a particle clump (the picture shows a 1-mm-wide region).

from the feedstock.

Table 2. Impurity Levels by GDMS

Element	Treated hi-B EG-Si	CZ from treated hi-B EG-Si	FZ from treated hi-B EG-Si
C	28.1	7.2	7.5
O	21.1	15.1	7.5
Al	0.24	< 0.005	0.042
B	0.36	0.34	0.36
P	0.10	0.054	0.073
S	< 0.04	< 0.04	< 0.04
Ca	< 0.007	< 0.007	< 0.007
Fe	< 0.005	< 0.005	< 0.005
Ge	< 0.004	< 0.004	< 0.004
K	< 0.007	< 0.007	< 0.007
As	< 0.002	< 0.002	< 0.002
Co	< 0.002	< 0.002	< 0.002
Cu	< 0.002	< 0.002	< 0.002
Ni	< 0.002	< 0.002	< 0.002
Zn	< 0.002	< 0.002	< 0.002
Cr	< 0.0005	< 0.0005	< 0.0005
Mg	< 0.001	< 0.001	< 0.001
Mn	< 0.0005	< 0.0005	< 0.0005
Na	< 0.001	< 0.001	< 0.001
Sr	< 0.0003	< 0.0003	< 0.0003
Ti	< 0.0006	< 0.0006	< 0.0006
V	< 0.0006	< 0.0006	< 0.0006
Zr	< 0.0003	< 0.0003	< 0.0003

The resistivity of a segment from treated high-B, EG-Si feedstock was 0.4 Ω-cm, p-type; CZ and FZ crystals grown from other segments of treated high-B, EG-Si feedstock also had resistivities of ~0.4 Ω-cm, p-type. Minority charge-carrier lifetime τ was measured by the photoconductive decay (PCD) method on the same segments and ingots using a 1064-nm light source. The treated feedstock had a lifetime of 0.3–0.9 μsec. The CZ ingots had lifetimes of 7–10 μsec (treated reject high-B, EG-Si feedstock) and 15–22 μsec (high-purity EG-Si feedstock), respectively, and the FZ crystal lifetime was 130 μsec. Table I also shows the solar cell efficiencies obtained for 1-cm^2 diagnostic solar cell devices fabricated on wafers cut from these materials. Table 3 gives additional cell parameters (open circuit voltage V_{oc}, shor-circuit current density J_{sc}, and fill factor FF) for these and for FZ and CZ commercial wafers that were similarly processed.

Table 3. Solar Cell Parameters

Sample Description	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	Efficiency (%)
As-Treated hi-B EG-Si	0.55	19.1	77.9	8.3
Baseline CZ From EG-Si	0.60	30.9	76.7	14.1
CZ from treated hi-B EG-Si	0.60	29.8	78.7	14.0
FZ from treated hi-B EG-Si	0.59	30.1	77.7	13.8
Commercial FZ Wafer	0.60	32.3	78.0	15.1
Commercial CZ Wafer	0.60	29.9	80.1	14.3

Diagnostic device I-V curves are shown in Fig. 4, and the corresponding internal quantum efficiencies, from which effective diffusion lengths were determined, are presented in Fig. 5. This small sampling of device performance indicates that devices made directly on gaseous melt-treated, reject, high-B, EG-Si feedstock have a little over half the efficiency of devices made from control CZ samples. Their internal quantum efficiency falls off with increasing wavelength. However, devices on CZ and FZ crystals grown from the Crystal Systems-treated feedstock have comparable PV performance (14.0% and 13.8% efficiency, respectively) to that of CZ control samples (14.1%).

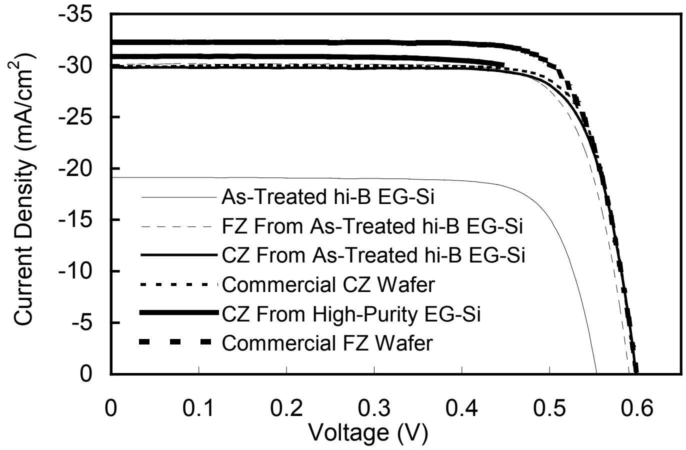

Fig. 4. Diagnostic solar cell I-V curves

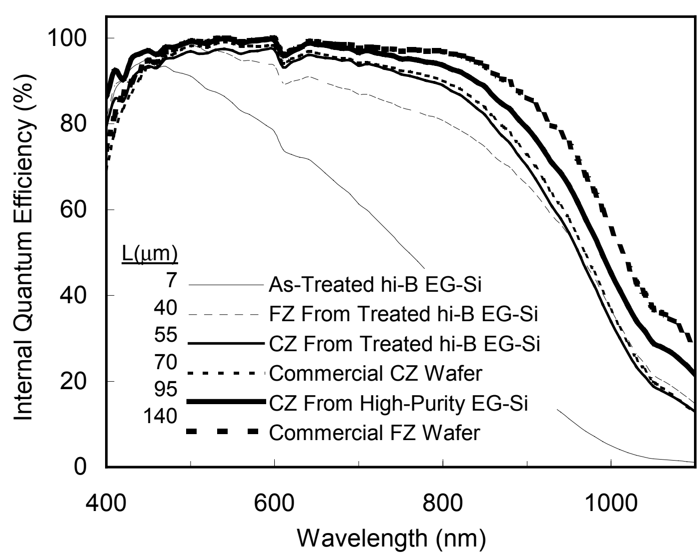

Fig. 5. Internal quantum efficiency and diffusion length for the cells of Fig. 4

SUMMARY AND DISCUSSION

FZ and CZ crystals were grown and characterized, and diagnostic solar cell devices were made, using a new type of SoG-Si feedstock developed by Crystal Systems—gaseous melt treated, high-B, EG-Si. Dislocation-free growth could be initiated by both methods. High feedstock carbon levels eventually supersaturated most of the melts and precipitated SiC particles. This is probably not a serious issue for multicrystalline growth methods, but it would be problematic for single-crystal growth. Additional efforts will be required to reduce the C content. The PV conversion efficiencies of 1-cm^2 devices made from CZ crystals we grew using the new feedstock (14%, AR-coated) were similar to those from CZ crystals we grew using EG feedstock (14.1%) and those we obtained using commercial <111> CZ wafers (14.3%). Devices with an efficiency of 8.3% were also made directly on wafers cut from the treated high-B EG-Si feedstock. The wafers were also successfully used as substrates for epitaxial Si thin-layer growth.

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[1] Chandra P. Khattak, David B. Joyce, Frederick Schmid, Ted F. Ciszek, Matthew R. Page, and Martha I. Symko-Davies, "Solar Grade Silicon for Solar Cell Applications," to be published in proceedings of the *17th European Photovoltaic Solar Energy Conference.*

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13. ABSTRACT *(Maximum 200 words):* This conference paper describes the Czochralski (CZ) and float-zone (FZ) crystals were grown from experimental solar-grade silicon (SOG-Si) feedstock materials developed by Crystal Systems. The materials were metallurgical-grade Si and highly boron-doped p-type electronic-grade Si (EG-Si) reject material, both of which were gaseous melt-treated to remove boron. Crystal growth observations, lifetime and impurity characterization of the grown crystals, and device performance of wafers from them are presented. Devices made directly on treated high-B EG-Si feedstock have a little over half the efficiency of devices made from control CZ samples. However, devices on CZ and FZ crystals grown from the treated high-B EG-Si feedstock have comparable PV performance (14.0% and 13.8% efficiency, respectively) to that of CZ control samples (14.1%).

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