Manufacturing Metrology for c-Si Photovoltaic Module Reliability and Durability

Part I: Feedstock, Crystallization and Wafering

Hubert Seigneur^{1,2}, Nahid Mohajeri^{1,2}, R. Paul Brooker^{1,2}, Kristopher O. Davis^{1,2,3}, Eric J. Schneller^{1,2}, Neelkanth G. Dhere², Marianne P. Rodgers^{1,2}, John Wohlgemuth⁴, Narendra S. Shiradkar², Giuseppe Scardera⁵, Andrew C. Rudack^{1,6}, Winston V. Schoenfeld^{1,2,3}

1. c-Si Division, U.S. Photovoltaic Manufacturing Consortium, 12354 Research Parkway – Suite 210, Orlando, FL 32826, USA
2. Florida Solar Energy Center, University of Central Florida, 1679 Clearlake Road, Cocoa, FL 32922, USA
3. CREOL, The College of Optics and Photonics, 4000 Central Florida Boulevard, Orlando, FL 32826, USA
4. National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Co 80401, USA
5. DuPont Silicon Valley Technology Center, 965 East Arques Avenue, Sunnyvale, CA 94085, USA
6. SEMATECH, 257 Fuller Road, Albany, NY 12203 USA

Corresponding Author: Hubert Seigneur, Hubert.seigneur@uspvmc.org

Abstract

This article is the first in a three-part series of manufacturing metrology for c-Si photovoltaic (PV) module reliability and durability. Here in Part 1 we focus on the three primary process steps for making silicon substrates for PV cells: (1) feedstock production; (2) ingot and brick production; and (3) wafer production. Each of these steps can affect the final reliability/durability of PV modules in the field with manufacturing metrology potentially playing a significant role. This article provides a comprehensive overview of historical and current processes in each of these three steps, followed by a discussion of associated reliability challenges and metrology strategies that can be employed for increased reliability and durability in resultant modules. Gaps in the current state of understanding in connective metrology data during processing to reliability/durability in the field are then identified along with suggested improvements that should be considered by the PV community.

Keywords

Polysilicon, Siemens, Fluidized bed reactor, Impurity, Czochralski, Ingot, Directional solidification, Crystalline silicon, Wafer, Kerfless, Light induced degradation, Crack, Shunt, Residual stress.

1 Introduction

Silicon, the most earth-abundant element in the periodic table after oxygen, accounts for 25.7% of the earth's crust and is mainly found as silicon oxides, in the form of silicate minerals. The production and purification of silicon dates back to the 1800s; however, current commercial methods were primarily developed in the 1900s. The process for making silicon substrates for PV cells can be divided into three different steps: (1) feedstock production, (2) ingot production, and (3) wafer production. Each of these

steps can in some way affect the final reliability/durability of PV modules in the field. Here we review each of these steps successively.

The scope for silicon feedstock production typically encompasses all processes needed to transform sand into polycrystalline chunks of silicon. These are in essence refining processes that are mainly classified in terms of grade or purity, process phase (metallurgical route, gaseous route, etc), cost, and energy consumption. This article reviews the majority of feedstock production processes used to create metallurgical grade silicon (MG-Si), upgraded metallurgical grade silicon (UMG-Si), and electronic grade silicon (EG-Si) before focusing on the main competing commercial technologies i.e. Siemens, fluidized bed reactor, and UMG silicon [1]. The Siemens and the fluidized bed processes account for the great majority of polysilicon used in crystalline silicon (c-Si) solar cell production.

The scope for ingot production includes techniques for monocrystalline silicon (mono-Si) such as the Czochralski (CZ) or float-zone (FZ) method, for multicrystalline silicon (multi-Si) such as casting and directional solidification DS, and for quasi-monocrystalline silicon (i.e. mono-like). Ingot production is mainly classified in terms of the resulting crystallinity of the ingot, which can be explained in terms of the grain size. Polycrystalline silicon, typically not used in PV applications, consists of a grain size on the order of nanometers (nm) to microns (μm). Multi-Si consists of grain sizes on the order of μm to millimeters (mm), while mono-Si occurs when the whole ingot is a single grain. Mono-like Si falls somewhere in between multi-Si and mono-Si. Typically, a Mono-like silicon ingot would consist of very large single grain occupying 60-80% of the total volume surrounded by multi-Si. These are not to be confused with nanocrystalline silicon (nc-Si) and microcrystalline silicon ($\mu\text{c-Si}$), which are forms of porous silicon that cannot be generated during ingot production. In fact, these have a paracrystalline structure, which consists of a mixture of small grains of crystalline silicon and an amorphous phase. Mono-Si CZ accounts for 40% of all c-Si solar cells while 60% are made from multi-Si according to the 2014 edition of the International Technology Roadmap for Photovoltaics (ITRPV www.itrpv.net). Reviews of silicon crystal growth for photovoltaics are available in the literature [2-4].

The scope for wafer production includes techniques for wire sawing such as slurry-based wire sawing and diamond-based wire sawing as well as kerfless wafering techniques such as the implant-cleave method, the exfoliation method, ribbon growth processes, and epitaxial growth processes. Today, most, if not all wafers used for crystalline silicon solar cells are produced using a wire sawing method. Reviews of wire sawing are available in the literature [5, 6]. According to the 2014 edition of the ITRPV, diamond wire sawing is expected to take over as the main wire sawing method in the near future.

This article is the first in a series dedicated to reviewing the impact of each processing step on PV module performance and reliability and identifying relevant metrology techniques that can be utilized to improve the quality and durability of the final product. The subsequent articles in this series have a focus in the areas of cell manufacturing (Part 2) and module manufacturing (Part 3). The focus of this article is the module manufacturing process (see Figure 1). The goals of this work are to:

1. Identify known failure modes and degradation mechanisms induced during manufacturing
2. Provide a review of the current state of metrology used during manufacturing for improved PV reliability and durability [7, 8]

3. Perform a gap analysis and identify where improvements can be made [9]

Figure 1. Depiction of c-Si PV manufacturing production areas across the supply chain highlighting feedstock, crystallization and wafering as the focus of this article.

2 Feedstock Production

The key for improving future c-Si module reliability and durability during feedstock production is being able to control the type and concentration of impurities present in the feedstock, which is process dependent, and doing so while maintaining or even reducing cost. Sensible metrology in process control and quality control can help in this regard. Ultimately, this is a convoluted challenge as crystal growth introduces new impurities as well as redistributes impurities existing within the polysilicon feedstock as a function of the growth technique, the furnace geometry, the heating scheme, and individual segregation coefficients of the various impurities. Introduction and redistribution of impurities occurs along the entire downstream manufacturing chain, from wafering processes, to cell fabrication, to module fabrication, and continues even after the modules are installed in the field (e.g. light induced degradation, etc). As a result, impurity control is very challenging. Nonetheless, this section on feedstock production aims to: (1) highlight the various processes (both conventional and unconventional) used to produce various grades of polysilicon and the impurity profile associated with each (where available); (2) increase the understanding of the redistribution that occurs in the impurity profiles between various grades of polysilicon and the resulting “usable” bulk material after crystal growth; and (3) recommend strategies for manufacturing metrology in the context of feedstock production. Understanding which impurities affect PV reliability and durability and being able to effectively measure critical impurity levels early in the process can be advantageous

In general, the grand challenges for feedstock production over the past few years have been to lower cost and energy consumption in kilowatt-hour per watt-peak (kWh/Wp), improve energy density in kilowatt-hour per kilogram (kWh/kg), improve gas/byproducts recycling and reuse, increase the purity to 7N (99.99999%) or higher, especially for solar grade polysilicon (SoG-Si) made from UMG processes, and unify and promote industry-wide adoption of materials standards and methodology for characterizing feedstock quality. In addition to increasing the purity, it is just as important, if not more important, to identify killer impurities versus impurities with only minor impacts. The impact of

impurities on cell and module performance increases for advanced architectures [10] and, contrary to popular belief, even if *n*-type substrates are used [11]. For example, chromium has been found to be extremely detrimental to *n*-type substrates, whereas Fe tends to be the problem for *p*-type. It has been reported [12] that the cost of feedstock produced by different feedstock production processes changes the cost of the c-Si modules by 11% for standard technologies and up to 7% for advanced technologies, conditional on maintaining the cell efficiency. If the cell efficiency cannot be maintained, then the low cost advantage of UMG-Si is lost due to quality degradation of 1.7% for a standard module technology.

Table 1 describes impurities currently specified in the PV industry standards (i.e. SEMI PV 017 standards) for solar grade feedstock:

Table 1. Impurities currently specified in industry standards for Solar Grade feedstock

Impurity Type	Element
Acceptor	B, Al
Donor	P, As, Sb
Atmospheric	O, N, C
Transition metals	Fe, Ni, Cu, Cr, Ti, Zn, Mo,
Alkali / Alkali Earth Metal	Na, Al, K, Ca

Additional relevant elements shown in the literature to have an impact [13-18], but they are without specifications in existing PV industry standards (i.e. SEMI PV 017 standards) are shown in Table 2.

Table 2. Elements that are impurities but have no specifications in existing industrial standards

Impurity Type	Element
Acceptor	In, Ga
Transition metals	Co, W, Nb, Au, Zr, V, Mn
Alkali / Alkali Earth Metal	Mg

2.1 Processes

2.1.1 Metallurgical Grade Silicon (MG-Si)

The methods for preparation of MG-Si, carbon and aluminum reduction are described in the following sections. Both have been implemented in the industry. However, because aluminum reduction produces a higher percentage of metallic impurities in the metallurgical material, carbon reduction has come to be the "process of choice" for producing MG silicon.

2.1.1.1 Carbon Reduction

MG-Si with a purity of 98-99% can be prepared by the reaction of high-purity silica with wood, charcoal, and coal in an electric arc furnace with graphite electrode (Eq.1). Silicon carbide (SiC) can form during this process, however, by keeping the amount of SiO₂ high, SiC can be eliminated (Eq.2).

MG-Si is contaminated with trace elements of metals such as Fe, Al, Ti, V, B, and P and compounds like SiC, SiN, and SiO₂, for example [19]. One of the main parameters, affecting the final yield of carbothermic process, is the quality of quartz raw material. Quartz is a naturally occurring mineral whose quality depends on the geographical location. Quartz material has to meet certain requirements to be

accepted for use in feedstock production regarding its chemistry, chunk size, mechanical strength, thermal strength, and softening properties [20]. Quartz contains impurities such as Al, Ti, B, P, Ca, and Fe, and inductively couple plasma-mass spectroscopy (ICP-MS) has been the method of choice for characterization of these impurities [20]. In general, the chunk size varies between 10-150 mm. The appearance of the raw material is tested macroscopically (size, color), microscopically (impurities, crystal structure, defects), by fluorescent light (microcracks), and cathodoluminescence (CL) microscopy (source material) [20]. Thermo-mechanical and mechanical properties of quartz are explored using the Elkem method (measuring heat, thermal strength, friability, and dust indices), the Spigerverket method (not common), and the Brazilian test for thermal stability [20].

2.1.1.2 Aluminum Reduction

The reduction of silica (SiO_2) by aluminum is a highly exothermic process (Eq. 3) and the heat of the reaction is adequate to sustain the reaction without any additional energy input. However, after formation of alumina (Al_2O_3), and in the presence of silica, the possibility of two side reactions exists, presented in Eqs. 4 and 5 (Note: The enthalpies are at 298K unless otherwise noted. As a result of this mixed temperatures, some enthalpies are not reported).

The formation of mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) and Al_2O_3 in these side reactions can be considered as yield reducers for SoG-Si production, as these minerals are not suitable for acid leaching .

2.1.2 Upgraded Metallurgical Grade Silicon (UMG-Si)

UMG-Si is MG-Si that has been further purified; but not quite to purity levels achieved with EG processes. The idea is to further improve metallurgical processes to achieve an acceptable purity level for the production of PV module and therefore avoid the need for costly chemical purification processes. When silicon feedstock (or polysilicon) has an acceptable purity level for the production of PV module, it is referred to as solar grade silicon (SoG-Si). SoG-Si is generally less pure than the polysilicon used for the electronics industry. The average reported energy consumption for UMG-Si is 30-40 kWh/Kg and average purity of 6N. The following sections describe several known UMG-Si manufacturing processes.

2.1.2.1 Elkem Process

The Elkem process has been mainly developed to reduce energy consumption, investment, and production costs of Si production. SoG-Si production via the Elkem process is a five step process that involves pyrometallurgical refining by adding calcium containing compound to molten silicon. These steps are: (1) smelter for MG-Si production; (2) slag treatment to remove B; (3) leaching by acids to reduce P and other metallic impurities; (4) directional solidification for further removal of impurities; and (5) post treatment by cleaning the bricks with acids. At the laboratory scale, the Elkem process consumes 25-30 kWh/kg energy.

2.1.2.2 Direct Carbothermic Reduction Process

Production of SoG-Si using the direct carbothermic reduction process has been pursued by projects such as SOLSILC and SPURT. This process uses plasma as the heating source for silicon reduction, followed by a unidirectional solidification. It requires ultrapure quartz and carbon black and it consumes four times less energy than the Siemens process, i.e. 25-30 kWh/kg of the product. One drawback of this process is the residual carbon in the final product originating from the reduction process [22].

2.1.2.3 Electrolysis Process

Since 2002, Chisso Corporation and NEDO have been actively engaged in research and development of Chisso SoG-Si (CSS), in which SiCl_4 undergoes an electrolytic reduction by zinc to produce 6N grade polysilicon (Eq. 6) [22].

In another approach, quartz is dissolved in HF followed by deposition of silicon on an electrode. The advantages of this approach are the elimination of carbon, lower process temperature, and deposition of very pure silicon from highly contaminated dissolved silicon [22].

2.1.2.4 SiF_4 -Na Process

SoG-Si production via SiF_4 -Na process was developed by SRI International. In this process, a source of Na ions (NaF) is added to H_2SiF_6 aqueous solution to form Na_2SiF_6 (Eq. 7). Thermal decomposition of Na_2SiF_6 yields SiF_4 and NaF, which is recycled back to the first step (Eq. 8). Through a melting or leaching process, the SiF_4 is reacted with Na to produce silicon and NaF (Eq. 9). A yield reducing parameter in this process is related to the formation of Si-O bond during thermal decomposition of Na_2SiF_6 , yielding solids such as SiO_2 or $\text{Na}_2\text{SiF}_n(\text{OH})_{6-n}$. These solids trap impurities and hence reduce the purity of the generated SiF_4 [23].

2.1.2.5 Directional Solidification (DS)

The DS technique takes advantage of silicon's higher solubility of most impurities in its liquid state as compared to its solid state. Using this approach, the uniformly distributed impurities will redistribute during the solidification process due to a majority of the impurities remaining in liquid phase and the solid silicon will be purified. Because P and B tend to be captured at grain boundaries, their removal from silicon using DS is almost impossible and hence other purification techniques have to be used. The size and crystallographic orientation of grains are important properties resulting from the solidification process. *In situ* and real-time X-ray imaging has been used to collect information on the grain structure and defects [24]. These methods can possibly play a role in the real-time control of the before-mentioned properties to improve both performance and reliability.

2.1.2.6 Electron Beam Melting

The State University of Campinas (UNICAMP) has been researching and developing a purification technique of MG-Si using an electron beam melting approach. The advantages of this technique are that their vapor pressures are higher than silicon and the use of a refrigerated copper crucible. The purity of final product has been reported to be 99.9995%, with B as the only element with the lowest extraction efficiency [22].

2.1.2.7 Photosil Process

An alternative approach to MG-Si purification is the Photosil process. In this process, metal impurities and P are removed by subjecting the liquid MG-Si to two consecutive segregation treatments. The first segregation process reduces the metal impurities and P concentration to result in a so-called UMG-1 (i.e., first treatment). The UMG-1 is then remelted and subjected to the secondary segregation process in which elements with small segregation coefficient are removed during solidification, resulting in solid UMG-2 silicon. The obtained UMG-2 solid silicon undergoes a plasma purification process in which the reactive species within an Ar plasma gas are able to volatilize impurities with large segregation coefficients such as B, C, Al, etc. An in-line ICP-OES (optical emission spectroscopy) is used to monitor the concentrations of elements such as B and P in the exhaust gas [25].

2.1.2.8 NEDO melt-purification Process

The NEDO melt-purification process of MG-Si involves a two stage process. The first stage consists of the removal of P and metallic impurities by directional solidification using electron beam equipment. For the second stage, B and C removal is carried out via plasma melting followed by a final metallic impurity removal by directional solidification [26].

2.1.2.9 Recycled Kerf loss Silicon

The total waste of high purity silicon during wafer slicing is greater than 40%. This kerf silicon loss contains silicon carbide and metals from the saw wire. Effective recycling techniques need to be developed as these particles are in μm and sub- μm ranges and, therefore, are hard to remove. Recently, Wang et al. reported a recycling technique based on nitric acid treatment to dissolve the metals followed by centrifugation to remove SiC [27]. The overall recycling yield was reported to be 45%.

2.1.3 Electronic Grade (EG)

EG-Si is mainly produced using the Siemens and Fluidized Bed processes, although other processes are discussed below. At first, scraps of EG-Si were used as the main feedstock route for SoG-Si. This was true before 2003 when total demand for SoG-Si was less than 10,000 tons/year. By 2005, the amount of EG scrap could not supply the demand for SoG-Si, so many companies started polysilicon production to meet the demand for PV [28]. Although EG-Si has the highest level of purity and hence capable of achieving close to theoretical efficiency (29%), its high cost/area and high processing-energy demand have been the main drawbacks. Therefore, over the past three decades, a great amount of research effort has been dedicated on finding lower cost processes for polysilicon production.

The four most-used polysilicon feedstocks for the production of EG-Si are silane (SiH₄), dichlorosilane (DCS, SiH₂Cl₂), trichlorosilane (TCS, SiHCl₃), and silicon tetrachloride (STC, SiCl₄). Currently, TCS, prepared from MG-Si, is the prevalent feedstock because of its favorable balance of manufacturing, purification, handling, and chemical reduction properties.

2.1.3.1 Historical Perspective

2.1.3.1.1 1950's

Siemens Process (Bell jar reactor). In the late 1950's the only two silicon purification processes in production were the Siemens process (leading) and the Komatsu process. Production of c-Si wafers, with high efficiency, requires high purity material. In the Siemens process, MG-Si is first reacted with hydrochloric acid to form trichlorosilane (Eq. 10). The distillation of TCS allows for most of the impurities to be separated. Using a batch process, inside a Siemens reactor, TCS is converted to solid polysilicon via a growth process on the surface of silicon filaments. The growth process is activated by high temperatures (≈1150 °C), which allows for the hydrogenation of the TCS and production of HCl as a catalyst. Eq. 11 shows the reaction of TCS conversion to polysilicon.

The Siemens process is highly energy consuming, with a major part of the energy being dispersed and lost. To avoid deposition on the inner surfaces of the reaction chamber, the walls have to be cooled and, therefore, up to 90% of the energy is wasted on the reactor walls. Currently, there are 13 global suppliers using the Siemens process. Major producers are Hemlock, Wacker, REC, GCL, Tokuyama, OCI and Mitsubishi.

DuPont Process (Fluidized bed reactor). The DuPont process was in pilot production at Texas Instruments and lab testing at MEMC. The DuPont process involves reduction of tetrahalosilane (SiX₄) or trihalosilane (SiHX₃) (where X could be chlorine, bromine or iodine) with H, Zn or Cd in a fluid or moving bed reactor. The process resulted in the formation of large quantities of amorphous silicon dust and explosive polymers when in contact with chlorosilanes.

Iodide Process (Seed particle or heated filament). The Iodide process was a lab study and has never gone into production. The production of silicon by using iodide process starts with a reaction between unpurified Si and I to form silicon tetraiodide (SiI₄) (Eq. 12) followed by purification (Eqs 13, 14) of tetraiodide via recrystallization, distillation and, finally, decomposition to high-purity elemental silicon and iodine [29, 30].

Komatsu Process (Bell jar reactor). The Komatsu process uses silane (SiH₄) in a Siemens-like bell jar reactor, rather than the TCS of the Siemens process. Komatsu would later acquire the Union Carbide

Corporation and combine their low cost silane ion-exchange separation of the union carbide process with its reactor technology.

2.1.3.1.2 1970's

In the 1970's, new silicon purification methods were introduced. Among these were the Union Carbide process and the Schumacher process.

Union Carbide Process (Free space reactor). The Union Carbide process is another approach that uses silane. It relies on a low cost silane ion-exchange separation of silane to be reacted in a free space reactor with subsequent consolidation via melting. But the free space/melting approach proved impractical. The use of SiH_4 as a feed allows for lower operational temperatures, higher conversion efficiency, and the elimination of corrosive byproducts [31].

Schumacher Process (Fluidized bed reactor). In the Schumacher process, the chlorinated silane or monosilane of Siemens and fluidized bed reactor (FBR) processes are replaced by brominated silane. Significantly lower processing temperatures in a continuous loop rather than a batch process have been recognized as the main advantages of Schumacher approach [32].

2.1.3.1.3 1980's

The 1980's saw a significant push for the fluidized bed processes in order to produce EG-Si faster and cheaper without sacrificing the purity. The JC Schumacher Company continued working on its promising Fluid Bed Reactor process based on tribromosilane. Texas Instruments also continued to develop a TCS fluid bed process during the 80's although the initial effort took place in the 60's.

Ethyl Corporation Process (Fluidized bed reactor). The Ethyl Corporation started to develop a Silane based Fluidized Bed Reactor (FBR) EG-Si process. Also referred to as the MEMC process today, this is a silicon purification approach in a sub-ppb range used for EG-Si. In this process, hexafluorosilicic acid (H_2SiF_6) is reacted with sodium aluminum hydride (NaAlH_4) to produce silane (Eq. 15). The produced silane is then decomposed (dehydrogenation, Eq. 16) in a FBR to Si and H [33]. The main yield reducing issues for the Ethyl Corporation process are reported to be the generation of fine powder and H adsorption into the polysilicon deposition layer [31].

H adsorption is the result of a low FBR decomposition temperature unable to break the more stable Si-H bonds. Consequently, when the hydrogen is released during melting, Si is splattered on the crucible and hot zone. The splatter can become a source of particles that later can cause loss of a dislocation free structure during crystal growth. Hydrogen can be significantly reduced by baking prior to melting.

2.1.3.2 Today's Methods of Choice

2.1.3.2.1 TCS Siemens Processes

Siemens CVD reactors have significantly evolved over time. Productivity has improved because of increased reactor size and pressure. A positive byproduct of increasing both the pressure and size of the

reactor has been significant decreasing electrical power consumption. As the demand for polysilicon grew, TCS capacity was increased specifically to support the polysilicon demand. Eventually, as the supply of silicon tetrachloride (STC), a by-product of the Siemens process, exceeded its demand, processes to make TCS from STC were developed. Two dominant technologies were developed to deal with the STC oversupply: STC converters (hydrogenation) and HydroChlorination (HC). Recently, STC is also being converted to high-purity silica.

2.1.3.2.2 TCS Siemens with STC Converters or Hydrogenation

The basic technology of STC converters is the hydrogenation of STC at ~1000 °C by the following reaction:

STC converters traditionally represented more production capacity than HC in the period from 1985 to 2005. Both technologies are being built into new facilities, but HC has become much more prevalent since about 2004.

2.1.3.2.3 TCS Siemens with HydroChlorination (HC)

The average reported energy consumption for TCS Siemens HC is 90-110 kWh/Kg for a purity of 9-11N. However, purity ranges from 6N to 11N depending on the supplier and the purification technology, experience in operation and investment in quality assurance and quality control methods. The experienced major suppliers can currently supply 11N for PV applications. HC is a continuous process where STC and hydrogen are contacted with MG-Si to form TCS at reaction temperatures typically >500 °C and pressures >20 bar:

The HC process is continuous and can operate a long time between shutdowns (more than a year). This is possible because impurities in the MG-Si become volatile and leave as gaseous reactor waste during the generation of TCS.

2.1.3.2.4 TCS Siemens with Direct Chlorination (DC)

The average reported energy consumption for TCS Siemens DC is 140 kWh/Kg and average purity of 9N. Similarly to HC, purity levels vary greatly and experienced major suppliers can deliver 11N using DC. This process is normally carried out in a DC FBR where finely ground MG-Si is reacted with HCl gas at about 300 °C and 2-4 barG. TCS is then purified by distillation steps.

The DC process results in impurities accumulating in the FBR and thus requires bed dumps every 6-10 weeks.

2.1.3.2.5 TCS Siemens with Pyrogenic Silica Production

The basic technology being pyrogenic silica production is to heat up STC in the presence of oxygen and hydrogen by the following reaction:

The produced silica can be recycled and used in the production of silicon while the HCl can be added to the DC FBR reactors to make TCS. It must be noted that using SiO₂ in the FBR reactor is not practical unless the SiO₂ is produced as granules of specific size rather than an amorphous powder.

Table 3. Comparison of the energy density for various TCS Siemens Processes

Method	Reaction Pathways	kWh/kg
Hydrogenation	$3\text{H}_2 + \text{SiCl}_4 \rightarrow \text{HSiCl}_3 + 3\text{HCl}$	-
HydroChlorination	$3\text{SiCl}_4 + \text{Si} + 2\text{H}_2 \rightarrow 4\text{HSiCl}_3$	90-110
Direct Chlorination	$\text{Si} + 3\text{HCl} \rightarrow \text{HSiCl}_3 + \text{H}_2$	140
Pyrogenic Silica	$\text{SiCl}_4 + 2\text{H}_2 + \text{O}_2 \rightarrow \text{SiO}_2 + 4\text{HCl}$	-

2.1.3.2.6 Silane Siemens

This upgraded version of Komatsu process produces the highest purity EG polysilicon today, 9N or more, with an average energy consumption of 157 kWh/kg. Initially, in the Komatsu method, high quality silane was obtained via the reaction of magnesium with MG-Si together at 500 °C in a hydrogen atmosphere to produce magnesium silicide (Mg₂Si). Then Mg₂Si was made to react with ammonium chloride (NH₄Cl) in liquid ammonia under 0 °C to make silane (SiH₄). This magnesium silicide process by Komatsu was terminated when production of silane by the HydroChlorination process was implemented at Union Carbide Corp in 1985. The magnesium silicide process was dropped because of higher cost and small production volume.

EG-Si can be then produced by the decomposition of silane via pyrolysis at 700-800 °C according to the following reaction:

2.1.3.2.7 Silane Fluidized Bed Reactor Process (FBR)

Polysilicon particles are produced by fluidizing silicon seed particles in a cone shaped reactor at a temperature above the decomposition temperature of a precursor gas, typically SiH₄. When particles reach a critical weight, they lose their upward drag force and settle at the bottom of the reactor. Polysilicon is also produced via the pyrolysis of silane (see Eq. 21). The FBR has an overall greater efficiency in use of reactant gases and at about 12-20 kWh/kg is less energy intensive with an average purity of 8N. REC boasted 4.1 kWh/kg in a 2012 Q1 report. However, temperature control between the reactant zone and the walls of the reactor is one of the main challenges of this process. Both MEMC (SunEdison) and REC produce polysilicon using Silane FBR technology.

2.1.3.2.8 TCS Fluidized Bed Reactor Process (FBR)

TCS FBR is also a lower energy process compared to Siemens. The deposition process relies on the following reactions:

Wacker, KRICT, AEP, SILIKEN are reported to experiment with TCS FBR polysilicon.

2.1.3.2.9 TBS Fluidized Bed Reactor Process (FBR)

The process begins by reacting metallurgical grade MG silicon with hydrogen and silicon tetrabromide (SiBr_4) to form a mixture of SiBr_4 and tribromosilane (SiHBr_3) which is separated and purified by distillation. The silicon deposition takes place according to the following reaction:

2.1.4 Summary of Impurity Levels for Various Silicon Feedstock Routes

Tables 4 and 5 show the accepted, specified, and achieved levels of impurities for SoG, UMG, and EG-Si from various feedstock routes, respectively.

Table 4. Accepted, specified, and achieved levels of impurities for SoG-Si from various feedstock routes

Element	MG-Si [19] ppm _a	Acceptable levels [34] ppm _a			SoG-Si (SEMI PV 017-0611)			
		p-type	Wafer	Feedstock	Grade I	Grade II	Grade III	Grade IV
Al	1200-4000				<1ppb _a	<20 ppb _a	<300 ppb _a	<1000 ppb _a
B	37-45				<1ppb _a	<20 ppb _a	<300 ppb _a	<1000 ppb _a
P	27-30				<1ppb _a	<20 ppb _a	<50 ppb _a	<720 ppb _a
Ca	590				<10 ppb _a	<50 ppb _a	<100 ppb _a	<4000 ppb _a
K					<10 ppb _a	<50 ppb _a	<100 ppb _a	<4000 ppb _a
Na					<10 ppb _a	<50 ppb _a	<100 ppb _a	<4000 ppb _a
Cr	50-140	4.7·10 ⁻⁴	4.8E-4	0.026	<10 ppb _a	<50 ppb _a	<100 ppb _a	<200 ppb _a
Cu	24-90	5.9E-3	0.046	4.6	<10 ppb _a	<50 ppb _a	<100 ppb _a	<200 ppb _a
Fe	1600-3000	9.7E-3	0.010	12.5	<10 ppb _a	<50 ppb _a	<100 ppb _a	<200 ppb _a
Mn	70-80							
Mo	<10				<10 ppb _a	<50 ppb _a	<100 ppb _a	<200 ppb _a
Zn					<10 ppb _a	<50 ppb _a	<100 ppb _a	<200 ppb _a
Ni	40-80				<10 ppb _a	<50 ppb _a	<100 ppb _a	<200 ppb _a
Ti	150-200	2.7E-4	2.7E-4	0.022	<10 ppb _a	<50 ppb _a	<100 ppb _a	<200 ppb _a
V	100-200							
Zr	30							
As						<20 ppb _a	<50 ppb _a	<720 ppb _a
Sb						<20 ppb _a	<50 ppb _a	<720 ppb _a
C					<0.3 ppm _a	<2 ppm _a	<5 ppm _a	<100 ppm _a
Mg								

Table 5. Accepted, specified, and achieved levels of impurities for UMG and EG silicon from various feedstock routes

Ele	UMG – Si	EG – Si
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	Photosil [35] ppm _a	NEDO [26] ppm _a	Carbothermic + two-step metallurgic [36] ppm _a	Combined metallurgic [37] ppm _a	SiF4-Na[23] ppm _a	Electron beam melting [38] ppm _a	CZ-Si from APIVT-Si [30] ppm _a	Recycled Kerf [39] ppm _a	Plasma purification of UMG [40] ppm _a	EG-Si ppm _a
Al	<2.1	<0.01	16.7±5	<0.01	0.14	0.44	<0.005	<0.05	<1.0	<0.0008
B	0.79	0.11-0.21	13±4	<0.59	0.08	19.2	4.16	1.28	1.3-5.3	<0.0002
P	0.91	0.03-0.13	7.3±2	0.06	0.05	0.35	6.80	1.54	9.1-18	<0.0008
Ca				<0.07		0.22	<0.007	<0.35	<0.7	<0.003
K						0.007	<0.007			
Na						0.06				
Cr			1.46±0.8		0.005		<0.001	<0.05		<0.003
Cu	<0.88		1.8±0.9	<0.002	0.004	0.13	<0.001	1.1		<0.003
Fe	<1	<0.025	13.6±4	<0.03	0.11	0.35	<0.005	<0.025	<0.5	<0.01
Mn						0.013	<0.001			<0.003
Mo					0.00		<0.001			<0.003
Zn					0.07		<0.002	<0.02		
Ni					0.00		<0.002	0.03		<0.01
Ti	<1.17	<0.006	1.75±1		0.13	0.05	<0.001	<0.006	<0.29	<0.003
V					0.00		<0.001			<0.003
Zr							<0.0003			
As				<0.02	0.00		<0.002			
Sb										
C							14.26		23-35	
Mg					0.53	0.02	<0.001	<0.06		

2.2 Reliability Challenges

In this section, potential PV reliability challenges are discussed for the two current industry relevant processes: Siemens and Fluidized Bed.

2.2.1 Impurities

The main long-term PV reliability challenge that can be tied to feedstock production is related to impurities. We consider the following potential sources of contamination during feedstock production using the Siemens process:

- The *graphite rods* that are used in thermal converters are sources of carbon contamination, but these are being replaced by the HC.
- The *graphite chucks* used to secure the polysilicon seed rods to the electrical contact in the baseplate of the reactor can be sources of contamination. Contamination is easily avoided if the entire chuck is removed before processing the grown polysilicon rod.

- *Polysilicon seed rod sections* that have been sawn or fabricated and used for the nucleation of TCS or silane gas and the resultant growth of a polysilicon rod can be a source of impurity. If so, chemical etching is used to remove surface contamination. In addition, advanced processing avoids sawing and grinding.
- The *purity of TCS* as well as the design of the TCS distillation and purification system.
- The *unpassivated surfaces* of tanks, valves, and pipes.

We consider the following potential sources of contamination during feedstock production using the FBR process:

- The failure of the *reactor wall coating* by cracking and spalling. Reactors are prepared by decomposing silane on SiC coated walls. The high purity Si coating works well as long as the SiC coating remains crack free and the Si coating does not spall.
- Metal contamination by repeated contact with *reactor pipes, valves, and under seed production*.
- Milling of granules for seed generation is another source of metal contamination [41].

2.2.2 Particle size and distribution (FBR)

Seeds and fine particles in FBR, due to their high surface areas, are more prone to oxidation, i.e. silicon dioxide contamination, and attraction of ambient elements such as carbon. The silicon dioxide solid particles are detrimental in the melt process as they cause dislocation formation. The multiplication and migration of these dislocations inhibit proper crystal growth [41]. The fine particles come from:

- Lack of surface stability for beads in TCS based fluidized reactors reducing silicon bonding to the surface and premature removal forming fine particles [42]
- Homogenous nucleation in silicon vapor, both from Silane or Trichlorosilane, produces vast quantities of sub μm diameter amorphous silicon dust [42, 43]. However, with Tribromosilane (TBS) used in the Schumacher process, growth is favored over nucleation so that no submicron amorphous silicon dust is produced.
- Clogging of the volume above the bed, also known as freeboard, with fine particles can further increase fine particles production. This is due to low temperatures in this zone, therefore inhibiting reactant gas decomposition.

2.2.3 Failure under operation

Four to five percent of polysilicon produced is also rejected for quality reasons including failure under operation such as:

- Aborted runs because of power failure
- Hot spot formation and filament burn out
- Broken or imperfect seed rods
- Gas inclusions and to non-uniform deposition at the joints
- Impure TCS, impure hydrogen
- Powder deposition on rod surface or included in the growth layer
- Contamination during rod processing

2.3 Metrology Strategies

2.3.1 Existing Metrology Techniques

Typical metrology carried out on feedstock prior to crystal growth consists primarily of elemental analysis. Impurity elements of interest were identified earlier in Tables 1 and 2. Available techniques to measure these impurities are [44]:

- Fourier Transform Infrared Spectroscopy (FTIR). FTIR provides interstitial O concentration and substitutional C concentration. Low temperature FTIR or photoluminescence (PL) can provide B, P and Al concentrations. FTIR cannot quantify O or C in precipitate form. Also, the reflectivity of the sample backside can introduce some error in the measurement.
- Neutron Activation Analysis (NAA). NAA is the most sensitive instrumental analysis technique and can make measurements on any form of feedstock. Unfortunately, results can take several months to obtain. Detection limits are not useful for dopant elements, which are usually present in high concentration.
- Inductively-Coupled Plasma Mass Spectrometry (ICPMS). ICPMS is useful to test for metals on the surface of any polysilicon form, such as chunks, granules, or powders. However, it is not able to measure the bulk impurity levels such as P, O, C, and N.
- Inert Gas Analysis (IGA) or Gas Fusion. IGA requires the feedstock to be shaped into a cylinder for insertion into the instrument. The sample is then heated such that gases (O, C, N, H) from the sample are emitted and analyzed.
- Glow Discharge Mass Spectrometry (GDMS). GDMS techniques can be used to quantitatively measure any elemental impurity concentrations in 6N pure (and higher) materials, in any form (wafers, chunks, granules, powder, etc). GDMS has poor detection limits for atmospheric species (O, C or N). It is most effectively used for the characterization of UMG-Si where a wide range of impurities are present. This is a direct sampling technique so there is no specialized sample preparation is required.
- Secondary Ion Mass Spectrometry (SIMS). SIMS is a fast and accurate technique that can measure all elements in any material form (wafer, chunks, granules, powder, etc), but is especially effective for dopants (B, P, As, Sb, Al, In), independent of electrical activity, and for atmospheric species (H, O, C, N), independent of their chemical state. This technique provides a more accurate quantitative measurement for impurities in SoG-Si at the sub-6N purity level. This is a direct sampling technique that does not require any specialized sample preparation.

Table 6. Comparison of the concentration limits for various elemental analysis techniques

Technique	Detection Limit
FTIR	100 ppm
NAA	10 ppb
ICP-MS	10 ppb
IGA	1 ppm
GDMS	10 ppt
TOF-SIMS	10 ppb
Dynamic SIMS	1 ppt

2.3.2 Metrology Techniques Beneficial for Reliability

Of the available metrology techniques, direct sampling using GDMS or SIMS are the most sensitive analytical methods available today for routine analyses of SoG-Si materials [45]. Table 7 summarizes useful feedstock metrology techniques for increased module reliability.

Table 7. Useful metrology techniques during feedstock production for increased module performance and reliability

Failure Mode or Degradation Type	Mechanism or Precursor	Metrology Method(s)
LID	O	Band-edge (BE) photoluminescence (PL)
		Deep-level PL [46]
		FTIR [47]
		Inert gas analysis [44]
OSF rings	Fe	Auger electron spectroscopy (AES)
		LIBS [48], FeB-pair splitting, GDMS [47]
		Secondary ion mass spectrometry (SIMS),
		Electron energy-loss spectroscopy (EELS) [49],
Shunts	B	LIBS [48]
		Band-edge (BE) photoluminescence (PL)
		Deep-level PL [46]
		FTIR [47]
Shunts	O precipitation	Inert gas analysis [44]
		Auger electron spectroscopy (AES)
		photoluminescence (PL), Deep-level PL [50],
		Laser-induced breakdown spectroscopy (LIBS)
Shunts	Cu contamination	[48], Glow discharge mass spectrometry
		(GDMS) [47]
		FTIR [51]
		Inert gas analysis [44]
Shunts	C	Auger electron spectroscopy (AES)
		LIBS [48]
		FeB-pair splitting
		GDMS [47]
Shunts	Fe	XPS/Auger, x-ray XPS [52]
		LIBS [48]
		XPS/Auger, x-ray XPS [52]
		FTIR [47]
Shunts	Ca	Inert gas analysis [44]
		Auger electron spectroscopy (AES)
		GDMS [47]
		GDMS [47]
Shunts	N	GDMS [47]
		Neutron activation analysis (NAA) [44]
		Inductively couples plasma mass spectroscopy
		(ICP-MS) SEMI MF1724 [44]
Shunts	High Z- impurities	X-ray fluorescence spectroscopy (XRF)
		Deep-level transient spectroscopy (DLTS),
		Electron spin resonance (ESR) [53]
Shunts	Metals on the surface	
Shunts	The electrical activity of traps	

2.3.3 Gap Analysis

Sampling strategy. The sampling strategy for feedstock analysis is important and must be carefully developed. Many elemental analysis techniques are expensive and/or take a significant amount of time. As a result, not every chunk, granule, or fines can be tested. A fast and accurate method, such as laser-induced breakdown spectroscopy (LIBS) could be useful [48].

FBR shortcomings. In order to overcome FBR shortcomings highlighted in the reliability challenges section, new reactor design including internal wall coating and alternative internal heating via microwave or favoring exothermic reactions have been suggested [41]. Perhaps metrology can play a role in assessing the condition of the internal wall coating, regulating temperature, and in monitoring in-situ particle size and distribution.

3 Ingot Production

During crystal growth, the impurity profile and material quality are significantly affected. New impurities are introduced, and existing impurities are redistributed. Thermal effects, impurities, and other factors (e.g. rotation speed, heat zone design, etc.) will affect the crystal quality and result in stress, point defect, twins, dislocation, grain, etc. Impurities and grain boundaries can combine to create defect clusters that can also have a detrimental effect. It is important to note also that the effects of impurities and defects are convoluted with other production areas (e.g. feedstock production, cell production, etc.). In this section, there is an attempt to decouple or isolate the ingot/brick production from other production areas. Ultimately, the noticeable degradation in performance and/or failure of solar cells and modules is the result of the aggregated effect of the changing impurities and defects profile throughout the entire manufacturing process.

In general, the grand challenges for ingot production over the past few years have been to optimize the hot-zone design to lower power consumption and increase ingot pulling speed; improve crucible and crucible coating quality to reduce impurities; control the uniformity of the dopant elements, especially phosphorus for n-type substrates; and recycle recovered Si effectively (both cropped pieces and kerf fines).

3.1 Crystal Growth Processes

Crystal growth may be split into the following classifications: monocrystalline, multicrystalline, and quasi-monocrystalline. The following sections detail manufacturing techniques for each of these crystal growth classifications.

3.1.1 Monocrystalline Processes

3.1.1.1 Czochralski Process (CZ)

3.1.1.1.1 Traditional CZ Growth

Traditional CZ growth involves the following steps: (1) filling up a crucible made of amorphous silica produced from an arc-fusion process using quartz with high purity polysilicon and calculated amounts of B or P dopant, (2) melting the Si in the crucible, (3) dipping a crystallographically oriented single crystal seed (typically <100>) into the melt, (4) withdrawing the seed crystal while rotating both the seed crystal

and the crucible in order to create and stabilize a cooler zone at the center of the surface of the melt by adding rotational driven convection to the thermal convection, (5) pulling fast at first to ensure a dislocation free crystal (this “dash” process reduces ingot diameter to a few millimeters), (6) decreasing the growth rate to increase the ingot diameter, and (7) significantly increasing growth rate to establish a cylindrically shaped crystal when near the required diameter. At the same time, the melt temperature is reduced to optimize growth rate for diameter control and productivity.

3.1.1.1.2 Continuous CZ Growth

The anticipated push towards n-type (higher lifetime) substrates in the PV industry has led to an increased interest in continuous CZ. Although often casually referred to as continuous CZ in the literature, it is in reality a continuous recharge CZ. A continuous supply of fresh polysilicon and dopant during growth results in long-body crystals and uniform resistivity, which is difficult, if not impossible, to achieve in traditional batch CZ growth. The ingot length is in principle determined by length of pull chamber instead of the crucible, hot zone, and puller tank size. As a result, productivity is increased. In practice, the ingot length is dependent on length of pull chamber plus volume of crucible, size of the hot zone and accumulation of impurities in the ingot. Disadvantages are increased process complexity, much longer run time, and a need for good purity feedstock. Furthermore, continuous CZ growth is also limited by the life of the quartz crucible and accumulation of dopants in the melt due to segregation coefficients. Crucible life may be 3 to 4 pulls, but 2 pulls per crucible is the current practical limit.

3.1.1.1.3 Magnetic CZ Growth

Magnetic CZ growth is similar to the traditional batch CZ growth; however, the growth is performed in the presence of a magnetic field. The magnetic field is applied to the melt for the purpose of disrupting convection currents that otherwise cause non-uniform incorporation of dopant impurities as well as oxygen and carbon in the growing crystal. It has been observed that, depending on the direction and magnitude of both the crystal and crucible rotational speed, the concentration of oxygen can be significantly reduced [54]. This is because the magnetic field reduces the surface contact of the melt with the walls of the crucible, so less oxygen is incorporated into the melt due to reduced dissolution of the quartz. There are several possible configurations for the time-dependent magnetic fields: a transverse magnetic field (TMF), a rotating magnetic field (RMF), or heater magnets, whether internal or external.

3.1.1.2 **Float Zone Process (FZ)**

The FZ process produces crystals with higher purity than the CZ process. One advantage of FZ is the potential of a near oxygen free crystal due to it being a crucible-free crystal growth process. FZ ingots can be purified from carbon and phosphorus by making several zone passes and concentrating impurities in the tail of the ingot. However, when using the FZ process, it is not easy to grow crystals with large diameters (i.e. >150mm).

3.1.2 Multicrystalline Processes

3.1.2.1 Casting

In casting, the melted raw material is transferred from its original crucible to another crucible for solidification. The crystallographic defects due to impurity precipitates have been studied by SEM, EDX, EBSD and EBIC [55]. Furthermore, scanning infrared polariscope (SIRP) has been used for characterization of residual strain distribution in casting ingot [56].

3.1.2.2 Bridgman technique

In the Bridgman method, one of the most well-established methods for crystalline Si ingot production, raw material is melted in a crucible followed by a cool down process to allow for crystalline growth. Different approaches for the cool down processes have been developed and practiced. In this section the pros and cons of each approach will be discussed.

3.1.2.2.1 Directional Solidification (DS)

The Bridgman DS method is primarily used for the production of multi-Si solar cells. In this technique, since the melt and crystals are in direct contact with the crucible, multi-grain growth becomes inevitable. Although the multi-grain phenomenon may be reduced by using a silicon nitride liner, these liners can also cause crystal contamination. Whenever a transition from single crystalline to multicrystalline is considered, the presence of grain boundaries (GB) and their nature is the main concern that needs to be addressed. It has been shown that large grained and columnar multi-Si, prepared via DS, is an acceptable, low cost alternative to CZ silicon, as long as the GB orientation is parallel to the carriers' diffusion path to the junction and the base contact [57].

The main drawback of the DS process is the use of a quartz crucible, which not only limits the size of the ingots, but also releases impurities such as silicon nitride. Furthermore, accumulation of a high level of impurities at the solid-liquid interface may inhibit DS growth and instead cause dendritic growth. Electron Beam Induced Current (EBIC) is one of the metrology techniques that has been used for contrast mapping of O, C, and N impurities in the GBs. Segregation of carbon and oxygen at the GB can be detected by FTIR and SIMS. Iron is one of the most common and harmful impurities in p-type mc-Si. In order to show iron distribution in mc-Si ingots grown by DS, Kvande et al. [58] have used multiple characterization techniques such as neutron activation analysis (NAA) and glow discharge mass spectrometry (GDMS). Synchrotron X-ray radiography (SXR) and synchrotron white beam X-ray topography (SWBXT) have shown to be effective in-situ imaging techniques to observe the real time dynamic evolution of the solid/liquid interface, its morphology, the interface velocity, grain orientation, and twinning or stresses throughout the solidification process [59].

3.1.2.2.2 Electromagnetic Casting (EMC)

Multi-Si manufacturing via EMC uses a cold crucible induction melting where an electromagnetic field is applied to melt metals without any contact to the crucible. This technique has been used in commercial production of ingots with nearly 1 ton weight in batch mode but continuous casting efforts have not shown much progress [60].

3.1.3 Gradient freeze technique (Quasi-monocrystalline Si)

This seed-assisted Bridgman technique produces single crystalline material that has advantages of both CZ and mc-Si, i.e. square, single crystal, low structural defect density, and low cost. This technique produces material with higher minority carrier lifetime and uniform lifetime compared to mc-Si [61]. While this material has shown a lot of promise, there are still major issues with defect clusters through significant parts of the brick [62, 63].

3.1.4 Optimization of ingot production

3.1.4.1 CZ Growth Optimization

Various challenges associated with CZ growth are listed below:

High oxygen (O) content. P-type CZ-mono wafers have high electronic quality, although they are known to suffer from light-induced degradation (LID) because of the oxygen content. The source responsible for oxygen in CZ silicon is quartz (SiO_2) crucible dissolution [64]. Most (> 98%) of the dissolved oxygen evaporates as SiO ; the remainder is incorporated into the silicon crystal. In order to reduce the O-content, strategies involve (1) using an alternative crucible material, (2) using a steady magnetic field, and (3) switching to a FZ process.

High C-content. The main sources of carbon are the graphite parts. An abnormal concentration is indicative of various and identifiable contamination paths [64].

Expensive equipment and process cost. In order to reduce costs, improvements in the hot zone's design (lower argon and power consumption, increase pulling rate) and the crucible (lower cost and longer lifetime) are needed. A 35% increase in the pulling rate was proposed through the optimization of the argon flow guide, the geometries of the radiation shield, and the side/bottom insulations [65]. By optimizing the original argon flow path, the heater and graphite susceptor lifetimes can be significantly lengthened. Changing the argon flow path prevents the graphite heater and SiO from reacting with graphite and forming silicon carbide, which deteriorates the heater and shortens heater's lifetime.

Process yield. Improvement of the yield can be achieved through charge increase. Increasing the charge can be done by using a larger crucible or using continuous charging. Since traditional crystal pulling is a batch process, the chamber for holding the crystal has a limited length. An approach is to have multiple charges, that is, after a crystal is pulled out and removed, without cooling down, the new material can be fed from the feeder. Continuous charging such as in continuous CZ is another option. Furthermore, particles are responsible for the formation of dislocations, which are detrimental to the yield. Therefore, particles due to crucible erosion and SiO_x deposits need to be prevented. Coating the crucible walls with a very small amounts of a barium compounds such as $\text{Ba}(\text{OH})_2$, BaCO_3 , BaO or Ba in solution in the Si melt causes the surface of the crucible to uniformly denitrify at crystal growth temperatures. The near perfectly smooth devitrified wall surface is considerably less likely to generate melt-borne particles when the dissolution of the crucible wall exposes bubbles and refractory oxide impurities.

Doping non-uniformity for n-type. The uniformity of the dopant can be improved through recharging strategies such as continuous CZ. Continuous CZ allows for metered dopant/poly introduction during crystal growth for "uniform" axial resistivity for both p-type and n-type ingots.

Strong turbulent melt power. The control of convective flow can be done using time-dependent magnetic fields: TMF, RMF, and heater magnets.

3.1.4.2 DS growth Optimization

Typical approaches to solve the various challenges associated with DS growth are:

Direct contact of crucible wall. Reduced contamination from the crucible wall may be achieved by improving the crucible coating or using an alternative crucible material.

Formation of Si_3N_4 and SiC precipitates. The strategy is to reduce contamination with N and C as well as improve the convective transport of N and C in the Si melt. This can be achieved by using better quality feedstock, careful handling of materials, and improving the stirring of the melt.

High contents of metal impurity. The approach here is to reduce the metal content, especially inside grain boundaries. Better purification of feedstock can help. Ultimately, advanced gettering strategies have to be identified.

High density of grain boundaries and related defects. A simple solution is to grow larger grains. This can be achieved by using a seed crystal and optimizing the growth process to minimize multi-grain growth and dislocations.

3.2 Reliability Challenges

3.2.1 Light Induced Degradation

Light induced degradation refers to the degradation of performance that occurs when a module is first exposed to sunlight as a result of carrier injection [66]. LID is attributed to boron (interstitial B_i and not substitutional B_s [67, 68]), oxygen (O_{2i}) and Fe. With respect to these impurities, there are two main lifetime reducing defects. One is the formation of boron-oxygen (B-O) complexes, mostly $\text{B}_i\text{-O}_{2i}$ [69]. The other is the interstitial iron formed when iron-boron pair (Fe-B) dissolves upon exposure to light [70]. Two important facts about LID are: (1) LID scales with the net doping and not the total B concentration and (2) the Fe-B defect is injection dependent whereas B-O complexes are not. Recently, even a low concentration of interstitial Cu, which has high solubility and diffusivity in silicon at room temperature, was observed to result in LID as well [71, 72].

LID greatly influences B doped CZ silicon growth (1–5% degradation) [70, 71, 73]. LID does not affect B doped FZ silicon wafers as much because of their low O content. Also, the effect of the B-O pair is not as critical in multi-Si cells (0.5–3% degradation) [70, 74–77]. Block casting results in typically higher concentration of impurities (metallic and others), grain boundaries, twins, dislocations, whose combined impact on lifetime degradation is greater in comparison to B-O pairs alone under sunlight [74, 78]. On the other hand, upgraded metallurgical-grade based multi-Si (UMG multi-Si) cells seem to be significantly affected by LID, especially at elevated temperature [70, 74–77] (0.5–10% degradation). Similarly, upgraded metallurgical-grade based mono-Si (UMG mono-Si), whether p-type (B-doped) or n-type (P-doped), suffers from LID [79] due to compensation from the B inherently found in high concentration in UMG Si in the latter case. UMG mc-Si is also affected at elevated temperature in the dark resulting in temperature induced degradation (TID). For instance, it was observed that UMG mc-Si

cell stored in the dark for 450 hours at 85 °C resulted in almost 6% power loss, and only half of this could be recovered in an annealing step [66].

LID is affected during various steps in the manufacturing process. The main processes that play an important role in LID are [70]:

- Feedstock quality (impurity concentration)
- Base resistivity and net doping
- Silicon crystallization (defect and doping distribution)
- Wafering and cleaning (surface contamination)
- Cell process (defect diffusion, gettering effects)
- Cell architecture [80]
- Passivation [81]

In order to mitigate LID, many approaches have been considered in the literature. Proposed strategies during ingot/brick production include:

- Avoiding the use of 1-2 Ω -cm B-doped CZ silicon (use high resistivity) [71, 82]
- Substituting B with Ga [82-84] although Cu and Ga resulted in LID [85]
- Substituting B with In was proposed [86]. Recently, In-doped Si was shown to exhibit LID as well [87]
- Reducing O content (e.g. by damping melt flows with magnetic fields) [82, 83]. However, an increase in cost and energy consumption is expected [86].
- Using n-type P-doped CZ silicon not produced from UMG [73, 79, 82, 83, 88, 89]
- Using quasi-monocrystalline silicon technology which has reduced O content. Also, dislocation rich Si, as in the case of quasi-monocrystalline silicon, results in an higher activation energy of B-O complexes [90].

Proposed strategies during cell fabrication include:

- Process optimization (tube furnace, belt furnace, rapid thermal annealing) [82]
- Using a SiC_xN_y antireflection (AR) coating. Carbon diffuses into silicon during contact firing and forms C-O dimers (CO_{2i}) instead of B-O_{2i} complexes [91].
- Using Al₂O₃ as a passivation layer [92]

Proposed strategies for post module fabrication consist of:

- Annealing at temperature above 200 °C for more than 30 minutes [81]
- Illuminating or applying a forward voltage to a device at an elevated temperature (100-200 kWh/m² at 60 °C [66] while [93] recommends temperatures above 90°C)
- Depositing a large negative charge onto the wafer surface [71]

Recent progress seems to indicate that LID can be separated into two components: surface and bulk LID. Although bulk LID can be fully recovered upon annealing, surface LID cannot. This is ascribed to the degradation of the SiN:H-Si interface and has been observed in low-Fe mono-Si and multi-Si cells alike [81]. In addition, Float-zone (Fz) samples as well as a-Si:H/c-Si (100) and a-Si:H/c-Si (111) interfaces have also been observed to deteriorate under light exposure while the Al₂O₃/c-Si (100) interface showed light-induced “improvement” [92]. This obviously would have important implications on passivation schemes as wafers/cells get thinner and surface recombination becomes even more critical.

3.2.2 Shunts

Shunts are localized short circuits in the PN-junction area or at the edge resulting in reverse currents, junction breakdown, and hot spots. Shunts can be divided into three types with respect to their origin: material-induced, process-induced, and field-induced shunts.

Sources of material-induced shunts are:

- Metal-decorated small-angle grain boundaries
- Si₃N₄ inclusions
- SiC precipitates

Sources of process-induced shunts are:

- Residues of the emitter at the edge of the cells
- Cracks (from high residual stress due to silicon solidification or other)
- Recombination sites at the cell edge
- Schottky-type shunts below grid lines
- Scratches
- Aluminum particles at the surface

Sources of field-induced shunts are:

- Large negative bias voltage

By far, most of the shunts are process-induced. However, we will focus only on material-induced and field-induced shunts in this section since it relates directly to crystal growth. First, *metal-decorated small-angle grain boundaries* are the result of crystal defects being decorated by impurities, and thus can be strong recombination sites leading to non-linear shunts similar in nature to edge shunts and scratches [94].

Si₃N₄ inclusions also result in shunts that have a nonlinear I–V characteristic (diode-like) [94]. Recently, it was observed that there were two types of Si₃N₄ inclusions resulting in shunts, monocrystalline Si₃N₄ fibers (less than 1 μm in diameter and several mm long) and hexagonally shaped Si₃N₄ crystallites (few tens of μm in diameter and several hundreds of μm long). Si₃N₄ coating on the surface of the crucible, which is used to reduce the residual stress in silicon, is the source for these inclusions. Furthermore, the residual stress in silicon resulting from the growth process is believed to play a role in the formation of SiC precipitates [95].

Lastly, *SiC precipitates* can likewise lead to strong ohmic shunts and are viewed as the most dangerous material-induced shunts [94]. These are due to C contamination from the graphite heaters in the crystallization furnace. SiC filaments are on the order of 1-3 μm in diameter. An SEM investigation shows that it is not the SiC precipitates themselves that represent the conducting channels but ring-shaped inversion channels around them [95]. The presence of SiC precipitates does not depend on the grain boundary type. Mechanical stress may play a role in the formation of SiC precipitates. Since the SiC grain boundary precipitates follow the interface morphology, they are obviously growing during or shortly after the crystallization process. Concerning crystal structures, block-casted multi-Si is strongly affected, especially wafers obtained from the top of the blocks/bricks. It was observed that SiC precipitates tend to migrate to the top of silicon blocks during casting. Good quality block-cast silicon solar cells can help mitigate this type of precipitate [95]. Field-induced shunts may appear under a large reverse bias of -5 to -20 V, especially in multi-Si cells.

3.2.3 Crystallographic Defects

Typical crystallographic defects are:

- Point defects - self-interstitials, vacancies, interstitial impurities such as oxygen, substitutional impurities such as dopants and carbon,
- Line defects - edge and screw dislocations, dislocation loops are created under the high stress conditions during thermal cooling, for example
- Planar defects - stacking faults come from the concentration of silicon self-interstitials, preferentially around nucleation sites (e.g. oxide precipitates, metal precipitates or mechanically damaged locations in the lattice)
- Bulk defects – Voids, oxide precipitates, swirls, interstitial and vacancy clusters, large dislocation loops

3.2.4 Cracks

- The thermal residual stress during casting can result in breakage of wafers and cells before, during, and after both solar cell and module manufacturing
- While elements such as O, C, or N can increase strength, it has been shown that precipitates made of these elements tend to create localized areas with significantly higher local stress and result in breakage
- Ingot and brick shaping can also result in crack initiation, which then can cause the wafers and cells to break. Equally critical are the edge roughness; polishing or etching of the silicon ingot prior to wafering process can increase the strength of the wafers by 33% [96, 97]

3.3 Metrology Strategies

3.3.1 Existing Metrology Techniques

Typical ingot parameters measured in-line prior to wafering consists of:

- Geometry (3D) e.g. Side lengths, phase lengths, diagonal lengths, angle, and flatness of the side
- Chamfers (3D)
- Detection of chipping, rills and other defects (3D)

- Surface roughness (3D), reflection
- Cracks, SiN/SiC inclusions
- PN / junction
- Lifetime
- Resistivity

Available techniques to measure these above mentioned parameters are:

- 3D inspection system. Inspection systems typically consist of halogen light within fiber glass and a camera.
- High resolution IR camera
- Photoluminescence
- Quasi steady state photoconductivity (QSSPC) or microwave detected photoconductive decay (μ -PCD)
- Laser optical line scanners (3D)

3.3.2 Metrology Techniques Beneficial for Reliability

Table 8 summarizes the techniques useful in predicting failure modes.

Table 8. Metrology techniques useful in predicting failure modes or performance degradation during crystal growth

Failure Mode or Degradation Type	Mechanism or Precursor	Metrology Method(s)
LID	Base Resistivity	GDMS/4-point probe [98] GDMS/ μ -PCD [98] GDMS/Hall measurement [98]
LID	Impurity segregation	Fourier transform infrared (FTIR) [99] Glow-discharge mass spectrometry (GDMS) [99] Laser-induced breakdown spectroscopy (LIBS) [48] Transmission electron microscopy (TEM) [98] Energy-dispersive spectroscopy (EDS) [98] Photoconductance (PC) [100]
Shunts	Impurity segregation	Fourier transform infrared (FTIR) [99] Glow-discharge mass spectrometry (GDMS) [99] Laser-induced breakdown spectroscopy (LIBS) [48] Transmission electron microscopy (TEM) [98] Energy-dispersive spectroscopy (EDS) [98] Photoconductance (PC) [100]
Shunts	Crystallographic defects	IR Transmission [99] PL Tomography [101] Electron backscattered diffraction (EBSD) [98] Photoconductance (PC) [100]
Cracks	Residual stress	Near infrared (NIR) linear birefringence [102]
Cracks	Edge roughness	Laser optical line scanners (3D)
Cracks	Imaging	IR Transmission Scanning Acoustic Microscope (SAM)

Cracks	Lifetime	RF-QSSPC [103] RF-PCD Infrared lifetime mapping Carrier density mapping [104] μ -PCD [103] PL [103, 105-107] PL Tomography [101] MD-PCD
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3.3.3 Gap Analysis

Metrology techniques for ingots/bricks potentially of interest that are not readily available are:

- 3D dislocation mapping. IR imaging can detect cracks and inclusions. PL can measure dislocations in a qualitative way. There still remains a need to develop a fast quantitative technique to measure dislocations in ingots. Infrared polariscopy is a viable candidate [ref].
- Residual stress imaging. Although Near Infrared (NIR) linear birefringence was demonstrated as a potential approach to map out residual stress within an ingot, this takes time. There is a need for a quick *imaging solution* for in-line metrology
- Visual inspection. Unlike CZ growth, the growth process in casting and DS methods cannot be observed in-situ through a port/window or a camera.

4 Wafer Production

Wafer production has also seen its fair share of challenges over the past few years. The main ones consist of the following:

- Reduction of kerf loss and kerf fine recycling
- Lowering cost (both traditional and kerfless approaches)
- Thin wafers handling and processing (e.g., limiting breakage)
- Unified incoming wafer specifications and standards
- Grain boundary passivation of multi-Si wafers
- Determination of electrical activity of crystallographic defects in a wafer
- Understanding critical crack lengths vs. wafer thickness
- Wafer consistency, especially in the case of multi-Si and quasi-monocrystalline wafers

4.1 Processes

Wafering, the process whereby the silicon wafer is formed from the ingot, is typically accomplished by traditional (sawing) techniques, or non-traditional (kerf-less) techniques. In the traditional technique, a mechanical saw is employed to cut the ingot, generating silicon dust (the “kerf”) from the location of the cut. In kerf-less technologies, the approach utilizes techniques that do not experience silicon waste. The following sections describe these two main classifications of wafering technologies.

4.1.1 Traditional Wafering

4.1.1.1 Slurry Wire Saw

Slurry-based multi-wire sawing is currently the main technique used to slice silicon ingots and bricks into wafers. Cutting is achieved by a combination of moving steel wires and a slurry consisting of abrasive particles (e.g. SiC) and a carrier fluid (e.g. polyethylene glycol). The slurry is brought to the steel wires through high flow-rate nozzles. Key factors are the wire speed, table speed, the solid fraction of SiC in the slurry, the slurry viscosity, and the size distribution and shape of the SiC particles.

Typically, silicon carbide (SiC) particles are used as abrasives. The volume fraction of solid SiC particles can vary between 20 and 60% and their mean grain size between 5 and 30 μm . The various abrasive size designations can be found elsewhere [108]. Polyethylene glycol (PEG) is normally used as the carrier fluid. Oil-based slurries have several disadvantages such as wafer singulation, cleaning, and disposal.

Surface damage shows maximum crack depths in the range of 10 to 20 μm . It was also observed that surface roughness and crack depth decreases from wire-inlet to the wire-outlet [109]. In addition, a lower abrasive concentration results in a thinner distribution of the fracture force and reduced roughness of the resultant wafers [110].

Recent progress in slurry wire sawing is the use of structured wires, which have the advantage of higher cutting speed and wire durability, thus reducing the cost, while at the same time not increasing the wafer surface damage [111].

4.1.1.2 Diamond Wire Saw

Unlike slurry-based sawing, which relies on loose SiC particles within a slurry as abrasives, diamond wire sawing relies on diamond particles metal plated onto a steel wire as fixed abrasives. There are important differences between slurry-based and diamond wire sawing methods:

- Surfaces of slurry-cut wafers tend to have more pits, while diamond wire-cut wafers exhibit scratches and microcracks. This happens especially when sharp diamond grits are used, resulting in a fracture rather than a ductile mode of cutting [112]. Additionally, there is a noticeable phase change [113] and increase in stress (both tensile and compressive - stress state varies across the surface of the wafer so both are present simultaneously but in different locations) on the wafer surface [114].
- The mechanical strength of wafers [115, 116] strongly depends on the surface morphology. Because cracks are produced along the wire direction in diamond wire-cut wafers, the failure strength of wafers along the wire direction is reduced compared to slurry-cut wafers, while it is increased in the direction perpendicular to the wire [113, 117].
- Additional benefits consist of a higher throughput, improved total thickness variation (TTV) [113], reduced Si surface contamination, and reduced cost [118, 119]. All of these are becoming more critical as the wafer thickness continues to decrease in industry.
- Saw damage removal etch and texturing remains to be optimized because of the complex surface properties and the presence of amorphous silicon [120].

Based on the many advantages described above, it is anticipated that diamond wire sawing will replace slurry based sawing in a near future with a market share >50% by 2020 according to the 2014 edition of the ITRPV.

4.1.2 Non-Traditional (Kerfless) Wafering

The surge in “kerfless” wafering methods in recent years sprung from an urgent need to reduce material cost/waste in the industry. Until recently, raw Si consisted of over 40% of the module cost, and stunningly, more than 50% of grown silicon ingots are wasted or recycled because of cropping, squaring, and wire sawing. While over 18 kerf-free wafering methods have been identified in another report [121], we here focus on the three main categories: solid phase, liquid phase, and gaseous phase processes.

4.1.2.1 Solid Phase Wafering

Solid phase wafering methods have the advantage of not requiring any changes in upstream silicon processing steps. Because these “cleave-layer based” wafering methods often require a specific crystallographic plane, mono-Si is the preferred substrate. Typical durability challenges with solid phase wafering are breakage, shunts, and stress due to the surface and sub-surface damage and micro-crack formation.

4.1.2.1.1 Implant-Cleave Processes

The implant-cleave technique is a two-step process as its name indicates. During the first step, a high energy hydrogen (proton) beam irradiates a thick silicon substrate. Because the protons all have the same energy, after propagating a certain distance proportional to their energy they come to a stop at the same depth and thus form a stressed cleave layer. The second step consist of an annealing step that results in cracks propagating along the stressed cleave layer as hydrogen is released from the substrate [121].

The energy of the proton beam determines the silicon wafer thickness. Implant energies of 1-4 MeV are typically used to produce wafers with thicknesses ranging from 20 μm to 150 μm [121, 122]. The depth of the surface damage is estimated to be about 10% of the target cleave layer depth, which is 20 μm for a 200 μm thick wafer, or 10 μm for a 100 μm thick wafer and so forth [122].

4.1.2.1.2 Exfoliation Processes

The exfoliation process relies on depositing a material with a different coefficient of thermal expansion (usually a metal or polymer) onto a thick silicon wafer. Depending on the deposition process, accumulation of hydrogen at the interface could also occur, which can help with the exfoliation process [123]. Subsequently, an annealing process takes place resulting in significant internal stresses at the interface and thus in the exfoliation of a foil substrate. Exfoliation processes are used at AstroWatt, IMEC (SLiM-Cut) [124, 125], and IBM [126]. A metal-based approach (e.g. nickel, nickel/chromium, silver/aluminum, etc. [127]) involves high temperatures resulting in silicon being ductile and, thus, poor foil quality due to plastic deformation. High temperatures can also increase contamination. A polymer-based approach (e.g. epoxy [127]) is advantageous due to the lower annealing temperatures, which are

well-within the brittle regime of silicon [53]. Recently, a single side heterojunction cell has been demonstrated using a 25 μm exfoliated c-Si foil with an efficiency of 12.5% [123] and 14.8%.

4.1.2.1.3 Laser Processes

Laser wafering [128] consists of focusing a laser at a particular depth in a silicon ingot, where a defect or pit is created on the order of the spot size. By rastering the beam across the entire subsurface of the ingot, a cleave layer is formed. An anisotropic etch or anneal steps can be used for cleaving individual wafers. Unlike ion implantation, more than one wafer can be created at one time as the laser can be focused at various depths with no damage to the silicon itself other than at the desired depth. Furthermore, a minimum thickness of 10 μm can be achieved while there is not any upper bound.

Another interesting laser process for wafering combines the concepts of using thin liquid-jet as waveguide for a laser and wet chemical processing step [129]. Water and KOH have been used as liquid carriers to enhance cutting via etching as well as removing any surface damage within a single step. The depth of surface damage was estimated to be on the range of 11 μm .

4.1.2.2 Liquid Phase Wafering

The silicon liquid phase wafering processes are also referred to as direct wafer processes. The liquid phase approach to wafering has been the most widely implemented kerfless method at the industrial scale because of its potential for high growth rate (E.g. About 1 mm per minute for horizontal ribbon growth HRG [130]). Solar cells made from liquid phase wafering methods have demonstrated efficiencies in excess of 16% [131]. Although many variations of liquid phase wafering have been considered, the most significant methods have proven to be silicon dendritic web growth (WEB), silicon edge-defined film-fed growth (EFG), string ribbon growth (SRG), and silicon ribbon growth on a substrate (RGS) [132]. The most recent variation is the direct wafer process from 1366 Technologies; efficiencies of 17% in customer trials have been reported using a standard cell line. Even though growing from the melt offers many advantages over standard wire sawing, mainly reduced material waste and cost, there are many disadvantages: high stress, high dislocation densities, multi-crystallinity, lowered contaminant segregation, all of which can present durability issues in terms of breakage and shunts.

4.1.2.2.1 Dendritic Web Growth (WEB)

Dendritic web growth relies on crystallographic and surface tension forces to form a web of silicon between dendrites during upward pulling. Typical characteristics are the formation of twins in central regions and thermal residual stress. Although twins are generally considered benign, residual thermal stress can result in the formation of crack and breakage. Because the material is mostly single crystal however, efficiencies above 17% have been reported for 4 cm^2 cells [133].

4.1.2.2.2 Edge Defined, Film Fed Growth (EFG)

Edge defined, film fed growth allows for a ribbon or even octagon tubes of crystallized silicon to be formed while it is being pulled from the melt through a graphite die. Typical defects for EFG wafers have grain boundaries, dislocations, intersecting twins stacking faults and high concentration of impurities (carbon, oxygen, and metals).

4.1.2.2.3 String Ribbon Growth (SRG)

Similarly, in the case of string ribbon growth, a silicon ribbon is formed between two carbon strings, which are pulled upward through holes in a flat crucible with molten silicon. Sovello AG has reported solar cells (untextured surface) fabricated using standard size string ribbon substrate with efficiencies of more than 16% [131].

4.1.2.2.4 Ribbon Growth on Substrate (RGS)

Ribbon growth on substrate is a high growth rate method that allows for the growth of a multi-Si wafer on a substrate which is pulled from the side of a casting frame full with molten silicon. Direct results of the fast growth are higher crystallographic defect densities (e.g. dislocations, grain boundaries) and impurities. Additionally, cell efficiencies tend to be lower than the other liquid phase wafering approaches, typically around 12% at best [134].

4.1.2.3 Gas Phase Wafering

4.1.2.3.1 Epitaxial (Epi) Growth Processes

Epitaxial growth processes require the use of appropriate substrates on which to grow a good quality epi layer (e.g. single crystal silicon wafer or other seed layers) as well as possibly a sacrificial layer (e.g. an oxide layer, ion implanted layer, or a porous silicon layer) [124]. Solar cell efficiencies up to 20.1% were recently obtained using a porous silicon sacrificial layer (SOLECEL) and 19.2% using an oxygen implanted layer (SIMOX method). Durability challenges may come from surface properties after separation and from the defect density in the epi-layer, which is related to the quality of the substrate. High defect density may play a role in breakage and shunts. Recently, it has been shown that porosity can be completely extracted from the epi-layer if high quality material and engineered macropores with large aspect ratios are used [135]. It turns out an epi-layer is not even needed since the carefully engineered macropores can be manipulated to exfoliate a high quality thin wafer from the thick substrate [136-138].

4.2 Reliability Challenges

4.2.1 Cracks and μ -cracks

Micro-cracking in wafers is inevitable, but micro-cracks do not have to induce catastrophic failure. Yet, micro-cracks and cracks can have an influence on the performance of solar cells [139, 140]. Typically micro-cracks (μ -cracks) will turn into cracks during cell/module manufacturing and beyond. In fact, cracks can grow in solar cells within a module due to mechanical loading and result in a degradation of performance [141-144]. On the other hand, cracks can result in catastrophic failure such as wafer or solar cell breakage, and others with potentially very serious consequences. In addition, localized hot spots due to micro-cracks can burn through silicon at over 1414 °C (2,577°F) and result in significant damage such as front glass cracks, crack shadows, worm tracks, snail trails, front or back bubble delamination, dead cell sections, internal arcs at over 8000 °C (14,000°F) and, even uncontained fires [145].

4.2.2 Breakage

There is a clear relationship between crack length and breakage [146]. Wafering is an important step in crack generation. The sawing process develops surface scratches and thickness non-uniformity which tend to lower wafer strength causing breakage [147]. SiC precipitates can cause sawing ditches and ridges to form on the surface of the wafer [148] and cause them to break during sawing. Residual stress, warping, when coupled to significant applied stress during cell/module manufacturing, can also result in breakage.

4.2.3 Warping

PV producers need their substrate to be flat from both a handling and material-printing process perspective. When non-flat substrates are handled in production, mechanical stress (e.g. screen-printing) can cause micro cracks to propagate to the point of failure during processing.

4.2.4 Shunts

Important shunting mechanisms:

- *Cracks causing short circuit.* Cracks created during wafering operations or subsequent fabrication steps can act as triggers to a tiny, intense hot spot during partial shading and reverse bias conditions.
- *Material inclusions like Si_3N_4 and SiC.* Such material inclusions occur during crystal growth.
- *Crystallographic defects.* The mechanical force applied onto a wafer during sawing can result in dislocation, pinholes, etc.

4.2.5 Stress

Stress is an important precursor to cracks and breakage. A clear correlation between residual stress during wafering and fracture strength of crystalline silicon wafers has been established [114]. Subsequent fabrication steps can introduce more residual stress and further reduce the fracture strength of crystalline silicon wafers [149].

4.2.6 Wire Failure

The presence of SiC clusters on the surface of the wafer can result in catastrophic failure of the wire [150, 151]. Si_3N_4 inclusions typically serve as nuclei for SiC precipitates. If a wire fails during wafering, the entire ingot is typically lost.

4.3 Metrology Strategies

4.3.1 Existing Metrology Techniques

Standard parameters that are measured on incoming wafers prior to solar cell fabrication consist of:

- Thickness, TTV
- μ -cracks, inclusions
- Saw marks, surface roughness
- Geometry
- Edge defects, chipping

- Bow
- Lifetime
- Resistivity
- Grain size
- Strain

The metrology techniques typically used to measure these parameters are:

- Eddy current displacement sensors
- Optical and laser sensors
- Capacitive sensors
- Laser micrometer
- 2D/3D profile sensors (scanner)
- Imaging (IR and Visible)
- Quasi-steady-state photoconductance (QSSPC)
- Photoconductance decay (μ PCD)
- Photoluminescence (PL) [61]
- Surface photovoltage (SPV)

4.3.2 Metrology Techniques Beneficial for Reliability

This section highlights existing or novel metrology techniques that would be useful in predicting failure modes:

Potential induced degradation. PID related shunts are associated with stacking faults including Oxygen-induced Stacking Faults (OSF) [152]. OSF-rings originate from oxygen precipitates that act as nucleation sites for stacking faults typically in CZ silicon. Typical characterization of stacking faults relies on the Wright etch, which is highly toxic. An attractive in-line alternative would be photoluminescence although it has some limitations [153-155].

Cracks and μ -cracks. Cracks are currently measured using IR imaging, which is quite effective. Attractive alternatives are photoluminescence (PL) and resonance ultrasonic vibrations (RUV), which is able to achieve measurement times close to 2 seconds per wafer to match the throughput of a typical production line. Although IR is limited by the diffraction limit, RUV is believed to be able to measure even smaller than 1 μ m [156]. Another exciting technique called 'edge-light' is quite sensitive and can be used with the ever versatile photoluminescence technique for crack detection. The advantage is the ability to detect much smaller cracks than possible with conventional equipment in multi-Si wafers [157].

Process induced shunts. Under reverse bias condition, early breakdown (Type 1 around -4 V to -5 V) is most likely due to surface cracks. A crack detection strategy similar to the one described in the previous paragraph would be of interest. Defect-related breakdown (Type 2 around -7 V to -13 V) is related to metal precipitates. A good impurity detection scheme and a clean wafering process are of interest. Two other valuable techniques are Laser-induced breakdown spectroscopy (LIBS) and photoluminescence (PL). Avalanche breakdown (Type 3 around -13 V to -15 V) is believed to be the result of deep-etch pits.

Reducing sub-surface damage during wafering together with the ability to characterize the sub-surface damage is important.

Residual stress. Stress can lead to wafer breakage during cell or module fabrication. Recent publications have shown a clear correlation between residual stress and the measured fracture strength of wafers before and after the damage removal etch [114]. Infrared polariscopy is a fast and non-contact method for in-line measurement of stress.

Light induced degradation. Useful techniques on incoming wafers would be Fourier transform infrared (FTIR), photoluminescence (PL) [158, 159], surface photovoltage (SPV) [160], and PC/PL [161].

Table 9 summarizes useful wafer manufacturing metrology techniques for increased module reliability.

Table 9. Useful manufacturing metrology techniques during wafer production for increased module reliability

Failure Mode or Degradation Type	Mechanism or Precursor	Metrology Method(s)
Doping Concentration	B-doping	4-point probe tester Eddy current probe Atom probe tomography Hall mobility measurements Laser-induced breakdown spectroscopy (LIBS) [48] PC/PL [161] Electron energy-loss spectroscopy (EELS) [162]
OSF rings	Defect	Wright etch [153] Secco etch [153] Copper decoration [153]
OSF rings	[O]	Fourier Transform Infrared Spectroscopy (FTIR) Secondary Ion Mass Spectrometry (SIMS) [163] Gas Fusion Analysis
OSF rings	Lifetime	Quasi-steady-state photoconductance (QSSPC) [164] Microwave photoconductance decay (μ PCD) Photoluminescence (PL) [154, 155] QSSPL [165] QSS- μ PCD [166]
Cracks		IR Transmission Imaging Scanning Acoustic Microscope (SAM) [167] Resonance ultrasonic vibrations (RUV) [167] Laser-induced ultrasonic pulses [168] Optical microscope/Mass Spectroscopy [169] Transmission electron microscopy (TEM) [170] Edge-light technique [157]
Cracks	Lifetime	Quasi-steady-state photoconductance (QSSPC) Microwave photoconductance decay (μ PCD) Photoluminescence (PL)
Cracks	Stress	Resonance ultrasonic vibrations (RUV) Micro-Raman Spectroscopy [171] IR Polariscopy [114, 172] X-ray Diffraction (XRD) Scanning Acoustic Microscope (SAM)
Crack	T, TTV, Bow	Shadow Moire [173] Eddy current displacement sensors

		Optical and laser sensors Capacitive sensors Linear inductive sensors Draw wire displacement sensors Laser micrometer 2D/3D profile sensors (scanner) Photoluminescence imaging [171] Nomarski optical microscopy [171] Fourier transform infrared (FTIR)
Crack	Oxygen	
Defect	Dislocation	Defect etching Scanning defect mapping system (SDMS) [174] Quasi-steady-state photoconductance (QSSPC) [164] Photoluminescence (PL) [106, 175-177] Scanning electron microscopy (SEM) [178] PVScan [179]
Defect	Lifetime	Transmission electron microscopy (TEM) [180] Quasi-steady-state photoconductance (QSSPC) Microwave photoconductance decay (μ PCD) Photoluminescence (PL) [175] Surface photovoltage (SPV) [160]
LID	Metal Impurities	X-ray fluorescence analysis (XRF) Energy Dispersive X-Ray Spectroscopy (EDX) [113] Cathodoluminescence (CL) Laser-induced breakdown spectroscopy (LIBS) [48] Photoluminescence (PL) [158, 159] Transmission electron microscopy (TEM) Surface photovoltage (SPV) [160]
LID	B-O Complexes	Surface photovoltage (SPV) [160]
LID	Lifetime	Quasi-steady-state photoconductance (QSSPC) Microwave photoconductance decay (μ PCD)
Shunts	Metal Impurities	X-ray fluorescence spectroscopy (XRF) Energy Dispersive X-Ray Spectroscopy (EDX) [113] Cathodoluminescence (CL) Laser-induced breakdown spectroscopy (LIBS) [48] Photoluminescence (PL) [158, 159] Vapor phase decomposition droplet collection (VPD-DC) [181] Total reflection X-ray fluorescence spectroscopy (TXRF) [181] Modified inductively coupled plasma mass spectrometry (ICP-MS) [181] Liquid surface etching (LSE) followed by TXRF [181] X-ray Absorption Near-Edge Spectroscopy (XANES) Infrared transmission microscopy (IRTM) [182]
Shunts	Inclusions, Precipitates	
Shunts	Lifetime	Quasi-steady-state photoconductance (QSSPC) Photoconductance decay (μ PCD) Photoluminescence (PL)
PID	Shunts / Stacking fault	Scanning electron microscopy (SEM) [152] Transmission electron microscopy (TEM) [152] Energy Dispersive X-Ray Spectroscopy (EDX) [152]

PID	SiN	ToF SIMS [152] Infrared transmission microscopy (IRTM) [182]
Wire Breaking	[C] in SiC	Fourier Transform Infrared Spectroscopy (FTIR) Secondary Ion Mass Spectrometry (SIMS) [163]
Wafering Damage	Surface Quality	Scanning electron microscopy (SEM) [113] Atomic Force Microscopy (AFM) Confocal laser Profilometer [109] Quasi-steady-state photoconductance (QSSPC) [183] Electron spin resonance (ESR) spectroscopy
Wafering Damage	Crystal phase	Raman Spectroscopy Electron backscatter diffraction (EBSD)
Grain	Physical Characteristics	Grain analysis system (GAS) [184] Scanning electron microscopy (SEM)
Grain	Orientation	Electron backscatter diffraction (EBSD) Optical methods [185] Photoluminescence (PL) [105, 186] X-ray Diffraction (XRD) IR Reflection
Grain	Electrical Activity ($\Sigma 3$ or twin GB – Electrically inactive) (Low angle GB – Electrically active).	Photoluminescence (PL)
Breakage	Failure Strength	Optical cavity furnace [179, 187]

4.3.3 Metrology Techniques for New Wafering Methodologies and Substrates

Evidently, the metrology strategy for wafering is highly dependent on the wafering methodology considered (i.e. traditional wafer sawing versus “kerfless” wafering).

Epitaxial silicon wafers. Measuring the concentration of B, the main doping impurity in p-type silicon, is not important for traditional wafering operations; however, such quality control measurements may prove necessary for creating a uniform porous silicon layer electrochemically since this requires the use of highly p-doped silicon substrates.

Implant / cleave wafers. Optical microscopy with heating a stage and mass spectroscopy are useful in characterizing hydrogen-implanted silicon used in the implant/cleave wafering scheme, and it was found that the amount of gas released when splitting the material is proportional to the surface area of microcracks [169]. Transmission electron microscopy has also been used in connection to the implant/cleave wafering scheme [170]. SIMS is used for characterizing the proton range distribution into the silicon [122]. Thermal and visible-light imaging techniques are used for temperature measurement and process control [122].

Thin wafers. It is expected that wafers are going to get thinner in the future. Coletti et al. describes that future devices using thin wafers will be more sensitive to impurity content than current state-of-the-art devices [10]. There is a need for cleaner materials and processes as well as fast and in-line metrology for impurity characterization. Using photoluminescence is certainly attractive [158]. An alternative would be laser-induced breakdown spectroscopy for the multi-elemental analytical characterization of silicon

samples; it is non-destructive, fast, highly sensitive to multiple elements, and does not require any sample preparation [48].

N-type wafers. The popular belief is that the n-type wafers for future novel architecture will ease the requirements on metallic impurities from a performance point of view. However, this is not the case when metallic impurities other than iron are considered [11]. It would be interesting to see what new reliability challenges arise with the use of n-type wafers. As these wafers become more prevalent, new metrology techniques sensitive to “killer impurities” in n-type wafers will need to be developed.

4.3.4 Gap Analysis

This section is intended to provide an assessment of the current state of understanding in being able to connect metrology data to reliability/durability in the field and identify areas of improvement that should be considered by the PV R&D community.

Stress Measurements. It is well understood that stress can lead to cracks, which are triggers for shunts, and that they can also propagate under thermal and mechanical loading, leading to reliability concerns including breakage. The stress levels inside wafers, whether tensile or compressive, are not routinely characterized on manufacturing lines if at all. There are certainly several interesting metrology techniques that can measure stress within wafers at line speed and therefore lend themselves very nicely to large scale manufacturing. Two examples are resonant ultrasonic vibrations (RUV) and infrared polariscopy (IRP) [114, 172]. Instead of measuring stress, a slightly different approach is to measure the stress budget by submitting an incoming wafer to an elastic stress similar in magnitude to the levels experienced during cell and module fabrication with the hypothesis that if the wafer survives the test, it is fit for fabrication. This is in effect the principle behind the optical cavity furnace proposed by the National Renewable Energy Laboratory.

Photoluminescence (PL). Photoluminescence is highly versatile and understandably gaining in popularity. Typically, carriers are excited above the bandgap (wavelength < 1100nm) using a laser at 800nm, and the photoluminescence signal is measured to detect several types of defects, whether structural (cracks/dislocations) or impurity related (precipitates), at line speed. However, there is much improvement that needs to be made in understanding the PL spectra and how it relates to various types of defects. Furthermore, PL might not be able to detect accurately certain defects. For example, Type A defects, although difficult to detect with PL, are more detrimental as they are known to exhibit Type II pre-breakdown behavior in reverse bias, resulting hot spots/shunts [188]. While alternative methods have been proposed [189], there is still a need for a metrology technique that can detect Type A defects.

Oxidation-induced stacking fault (OSF) rings. OSF-rings are difficult to characterize before oxidation. They not only affect performance, but they also can affect reliability. The key is to detect the border region between silicon self-interstitials (outside the ring) and vacancies (inside this ring). Photoluminescence and other in-line techniques are not very good at detecting this region although it is possible [153]. Currently, only off-line techniques such as Cu-decoration, Secco etch, and Wright etch can do a satisfactory job. There is a need for an in-line metrology that can identify regions between silicon self-interstitials and vacancies.

Epitaxial silicon (Epi-si) wafers. Epi-si wafers are also gaining in popularity recently. An adequate measurement of porosity in the porous layers in a high through-put environment would be useful. The characteristics of the porous layer are important in order to properly release the free standing epi-layer from the parent substrate with high yield.

Diamond wires. Diamond wires are becoming more and more popular. SiC clusters formed during multi-crystalline ingot growth can result in wire breakage. Also, the wires are continually decreasing in diameter in order to reduce the kerf loss and support the trend of decreasing wafer thickness, which in turn increases the chances of the wire breakage. Thus, monitoring the level of wear in the diamond wires is critical. If the wire breaks during sawing, the entire ingot is lost. Furthermore, it was noted in the case of slurry wire sawing that the wire tension in the wire web is lost during ingot cutting. Perhaps the use of metrology to monitor the wire tension would be useful as well [190].

High-speed evaluation of crystal structure/orientation. There are some advantages in measuring crystal structure and orientation for mono-Si wafers as well as grain size and orientation for quasi-monocrystalline and multi-Si wafers. This information is useful in determining the quality of the damage etch removal, or in determining the appropriate chemistry for texturing, or again the appropriate recipe for the passivation of solar cell surfaces.

In-line minority carrier lifetime measurements. It is desirable to have a high-throughput lifetime measurement on as-cut wafers, and being able to separate lifetime due to bulk vs. surface recombination.

High speed/real-time identification of areas with high defect density. Determining the structural defect density (SDD) usually takes hours and relies on etching and laser scanning. PL is much faster; however, it is believed that PL is not well equipped to detect type A defects after antireflection coating (ARC) and prior to cell processing [191]. Recently, a new proposed approach relies on chemical treatment and image processing, boasting minutes as opposed to hours of processing time [189]. Even shorter processing times would be desirable.

Scan density during inline inspection of wafers. Determine optimal scan density and cost versus need (value-cost curve). This would help also in evaluating the uniformity of wafers from different polysilicon sources, ingots, bricks, etc.

Methodology for surface (metal) contaminants. This is more important with new cell architectures. Methods for determination of surface metal contamination have been well established for mirror polished wafers in the microelectronics world; however, they cannot be easily applied to PV wafers because of the large roughness. The following methods have been proposed for PV: vapor-phase decomposition droplet collection with total reflection X-ray fluorescence spectroscopy (VPD-DC-TXRF), a modified inductively coupled plasma mass spectrometry (ICP-MS) for non-polished wafer surfaces, and liquid surface etching (LSE) followed by TXRF analysis. There is a need for a fast and in-line method to characterize the quality of a wafer surface before cell fabrication [181].

Compensated doping. There may be a need to measure all dopant concentrations in addition to just resistivity, desirably in-line and using full wafer mapping. It was demonstrated that the initial degradation of solar modules seemed to be influenced by the silicon feedstock (in this case SoG-UMG)

used in wafer production; while the long term degradation mechanisms seemed not to be [192]. LID could be permanently deactivated for SoG-UMG [193]. Furthermore, uneven distribution of dopants has been shown to have a remarkable effect on the residual stress and therefore breakage [194].

5 Summary and Conclusion

The process steps for making silicon substrates for PV cells include feedstock, ingot, and wafer production. The final reliability/durability of the PV modules in the field can be impacted during or as a result of each of these process steps. It is desirable to identify metrology techniques that can be performed during manufacturing to predict failures or unacceptable degradation for PV modules in the field.

5.1 Feedstock Production

Several different failure modes can develop during or as a result of the feedstock production processes. When a fluidized bed reactor (FBR) is used, seeds and fine particles can form, which can result in the formation of dislocations and inhibit proper crystal growth, and can negatively impact durability. However, the major reliability challenge that can occur as a result of the feedstock production processing step is the presence of impurities. Depending on the process used, there are several different sources of impurities. Where possible, impurities and their accepted levels for solar grade silicon have been identified in this article.

Prior to crystal growth, the typical metrology carried out on feedstock involves elemental analysis. Although many characterization techniques have proven to be useful in predicting potential future reliability challenges, direct sampling using glow discharge mass spectrometry and secondary ion mass spectrometry have been identified as the most sensitive analytical methods available today for routine analyses of PV grade materials. Because many elemental analysis techniques are expensive and/or take a significant amount of time, it is not possible to examine every chunk, granule, or fines. Therefore, a fast and accurate method, such as laser-induced breakdown spectroscopy could be useful. In addition, to overcome FBR shortcomings, new reactor design should be investigated.

5.2 Ingot Production

Ingot production processes can result in many different types of failure modes. Depending on the grade of silicon, LID is a major reliability challenge that can result from ingot production, with UMG mc-Si, and UMG mono-Si being the most susceptible. Several steps have been taken to mitigate LID during cell fabrication and post module fabrication. Crystallographic defects and material-induced and field-induced shunts are other reliability challenges that can occur as a result of ingot production. Several of the processing steps in ingot production can also result in crack formation, which will also impact reliability and durability.

Several metrology techniques to predict the failure modes that occur as a result of ingot production exist. To predict LID, metrology techniques focus on identifying levels of B (or other dopant) and O via the measurement of the base resistivity, net doping, and impurity segregation. Metrology techniques to predict shunt formation identify phenomena including impurity segregation and crystallographic defects. Cracks are identified by examining residual stress, edge roughness, imaging, and lifetime.

There are several types of metrology techniques that could be potentially useful for identifying failure modes that are not currently available and should be developed. A fast, quantitative method of measuring dislocations in ingots is desirable for 3D dislocation mapping. A fast imaging solution for in-line metrology is also needed for both residual stress imaging and visual inspection.

5.3 Wafer Production

Many reliability issues can occur as a result of wafer production. Stress induced during wafering can result in cracks and breakage. Micro-cracking in wafers is unavoidable, and its impact on durability can range from minor to catastrophic failure, including wafer or solar cell breakage and shunt formation. Breakage can also be caused by scratches, variations in thickness, ditches formed by SiC precipitates, residual stress, and warping. Shunting can result in hot spots formation, which can have severe impacts on module durability.

Numerous metrology techniques exist for the characterization of failure modes that can result from wafer production. Cracks can be characterized using IR imaging, photoluminescence, and resonance ultrasonic vibrations. Residual stress can be evaluated in-line using infrared polariscopy.

There are several areas where improvements could be made to metrology techniques that could improve the connection between wafering steps and PV module reliability/durability, for both traditional and new wafer processes. For example, with new cell architectures, in-line methods to determine surface metal contamination of PV wafers must be developed. Proposed methods include VPD-DC-TXRF, ICP-MS, and LSE-TXRF. In addition, although stress developed during wafering can trigger many reliability concerns, it is not routinely characterized on manufacturing lines. Metrology techniques that can measure stress within wafers in line, such as RUV and IRP could be useful in predicting field durability as a result of wafering.

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5.5 Glossary of Acronyms

Acronym	Definition
Al	Aluminum
AES	Auger electron spectroscopy
AFM	Atomic force microscopy
ARC	Antireflection coating
As	Arsenic
Au	Gold
B	Boron
C	Carbon

Ca	Calcium
Cd	Cadmium
CL	Cathodoluminescence
Co	Cobalt
Cr	Chromium
c-Si	Crystalline silicon
Cu	Copper
CZ	Czochralski
DC	Direct Chlorination
DCS	Dichlorosilane
DLTS	Deep-level transient spectroscopy
DS	Directional Solidification
EBIC	Electron beam induced current
EBSD	Electron backscattering diffraction
EDX	Energy dispersive X-ray spectroscopy
EELS	Electron energy-loss spectroscopy
EFG	Edge-defined film-fed growth
EG-Si	Electronic grade polysilicon
EMC	Electromagnetic Casting
Epi-si	Epitaxial silicon
ESR	Electron spin resonance
FBR	Fluidized bed reactor
Fe	Iron
FTIR	Fourier transform infrared spectroscopy
FZ	Float Zone
Ga	Gallium
GB	Grain boundaries
GDMS	Glow discharge mass spectrometry
H	Hydrogen
HC	HydroChlorination
HF	Hydrofluoric acid
HRG	Horizontal ribbon growth
ICP-MS	Inductively couple plasma-mass spectroscopy
ICP-OES	Inductively couple plasma-mass spectroscopy
In	Indium
IR	Infrared
IRP	Infrared polariscopy
IRTM	Infrared transmission microscopy
ITRPV	International Technology Roadmap for Photovoltaic
K	Potassium
LIBS	Light induced breakdown spectroscopy
LID	Light Induced Degradation
Mg	Magnesium
MG-Si	Metallurgical grade polysilicon
mm	Millimeter
Mn	Manganese
Mo	Molybdenum
Mono-Si	Monocrystalline silicon
Multi-si	Multicrystalline silicon
N	Nitrogen
Na	Sodium
NAA	Neutron activation analysis

Nb	Niobium
nc-Si	Nanocrystalline silicon
Ni	Nickel
nm	Nanometer
O	Oxygen
OSF	Oxygen-induced stacking faults
P	Phosphorus
PEG	Polyethylene glycol
PL	Photoluminescence
PV	Photovoltaic
QSSPC	Quasi-steady-state photoconductance
RGS	Ribbon growth on a substrate
RUV	Resonance ultrasonic vibrations
SAM	Scanning Acoustic Microscope
Sb	Antimony
SDD	Structural defect density
SEM	Scanning electron microscopy
SiC	Silicon carbide
SIMS	Secondary ion mass spectrometry
SoG-Si	Solar grade polysilicon
SPV	Surface photovoltage
SRG	String ribbon growth
STC	Silicon tetrachloride
SXR	Synchrotron X-ray radiography
TBS	Tribromosilane
TCS	Trichlorosilane
TEM	Transmission electron microscopy
Ti	Titanium
TID	Temperature induced degradation
TTV	Total thickness variation
UMG-Si	Upgraded metallurgical grade polysilicon
UNICAMP	State University of Campinas
μ-cracks	Micro-cracks
μc-Si	Microcrystalline silicon
μPCD	Microwave photoconductance decay
V	Vanadium
W	Tungsten
WEB	Dendritic web growth
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence spectroscopy
Zn	Zinc
Zr	Zirconium

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