

Progress in n-type monocrystalline silicon for high efficiency solar cells

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ABSTRACT

Future high efficiency silicon solar cells are expected to be based on n-type monocrystalline wafers. Cell and module photovoltaic conversion efficiency increases are required to contribute to lower cost per watt peak and to reduce balance of systems cost. Past barriers to adoption of n-type silicon cells by a broad base of cell and module suppliers include the higher cost to manufacture a p-type emitter junction and the higher cost of the n-type mono silicon crystal. Technologies to reduce the cost of manufacturing the p-type emitter by diffusion or implantation of boron are being developed in the industry. To reduce the cost and improve further the quality of n-type mono silicon crystal, SunEdison has developed a continuous Czochralski (CCZ) crystal pulling process, based on the technology of Solaicx, acquired in 2010. This CCZ technique allows production of a crystal with much greater resistivity uniformity, with a lower incorporation rate of lifetime-reducing metals impurities, and allows crystal oxygen to be selected independent of production batch size. CCZ is expected to reduce n-type crystal cost below that of current p-type mono crystal.

Advantages of silicon as a solid state material

Silicon, although an indirect band-gap element, has several advantages which have made it the primary material for semiconductor and photovoltaic applications. It is made into a conductor by measured addition of a small amount of electronic impurities, such as boron. It exhibits an acceptable (indirect) band-gap, carrier mobility, bulk minority carrier lifetimes and other electronic properties. It grows a very stable native oxide, allowing the protection and passivation of interfaces. Silicon crystals can be grown threading "dislocation-free" (DF) in large sizes (meters in length and up to 450mm in diameter). The fact that single crystals can be grown threading DF enables the agglomeration of chemical and native point defects into specific bulk micro-defects not possible in materials possessing dislocations. Some of these defects can be advantageous in semiconductor manufacturing (oxygen defects used for internal/intrinsic gettering of process-added impurities) and some unwanted (oxygen clusters and precipitates which are physical recombination centers, reducing lifetime). Silicon is abundant; it is the second most common element in the Earth's crust, bound in silicates. The cost of the purified raw material – solar or electronic grade polysilicon – is relatively low and can be bought in high purity in large volumes. Finally, silicon technology for solar cell materials benefits from over 50 years, sustained investment in research and development by the semiconductor silicon industry.

Monocrystalline silicon wafers show very high minority carrier lifetimes compared to multicrystalline wafers, due to the absence of grain boundaries, dislocations, electrical-active decorated metals on those structural defects and excessive background metals; these defects in multicrystalline silicon reduce photovoltaic conversion efficiency due to the many types and large density of carrier recombination centers.

Advantages of n-type monocrystalline silicon

The champion silicon photovoltaic conversion efficiencies, without stacked multi-junctions or concentrators, have been demonstrated on n-type Heterojunction with Intrinsic Thin layer (HIT) and inter-digitated back contact (IBC) cells [1, 4, 6]. In 2013, Panasonic produced a record 24.7% cell conversion efficiency using its HIT architecture on a thin (98 μm) cell with a surface area of 101.8 cm^2 [2]. Panasonic's 2013 production cell efficiency, using a similar earlier generation architecture, has been independently estimated as 21.6%. In 2012, Sunpower demonstrated 24.2% using its third generation "Maxeon" IBC cell, and offers modules with up to 20% efficiency [3, 6]. An IBC cell must be fabricated using silicon wafers with a large minority carrier diffusion length, for all the charge carriers to reach the emitter, since the p-n junction is deliberately located at the rear of the cell.

N-type silicon exhibits a stable, high minority carrier lifetime [6, 17]. Diffusion lengths of minority carriers (holes) in n-type silicon are much

higher than for electrons in p-type silicon. N-type silicon does not exhibit light induced degradation seen in p-type silicon, allowing increased values of stabilized cell efficiency. Light induced degradation (LID) is an immediate, light activated reduction in material bulk minority carrier lifetime leading to lower photovoltaic conversion efficiency. LID has been shown to be a strong function of boron and oxygen concentration [5]; in p-type silicon, boron is the impurity deliberately added to provide electrical resistivity. In p-type monocrystalline silicon, the initial conversion efficiency can be reduced by 0.5-3% (relative) by LID, due to the boron and oxygen defect effect on lifetime. Since the reduction is to a value of lifetime set by the boron-oxygen defect concentration in the crystal, as advanced devices are made which allow higher initial lifetimes due to reduced surface recombination, the decrease due to LID is even more evident. N-type silicon avoids this condition as no appreciable concentration of boron is present (oxygen concentration may be the same as for p-type ingot).

N-type silicon exhibits a higher lifetime tolerance for most common bulk metallic impurities (e.g., Fe) [6, 9]. Tolerance for Co and W was also demonstrated. This led to an early expectation that n-type mono silicon would be relatively impervious to metals addition, but this is not accurate. Certain impurities and defects can decrease lifetime in n-type silicon (e.g., Cr). Cr can affect n-type cell efficiencies at concentrations as low as 10^{10} atoms/ cm^3 [16]. Cu can also strongly reduce the lifetime of n-type silicon, similar

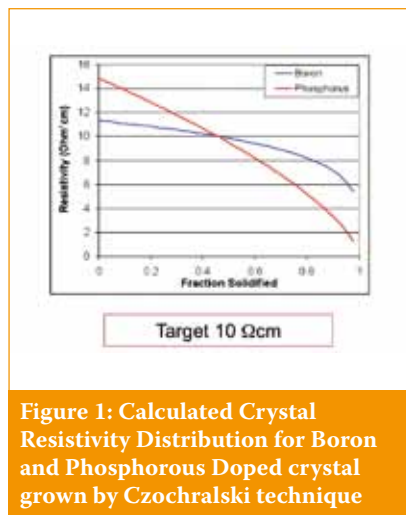


Figure 1: Calculated Crystal Resistivity Distribution for Boron and Phosphorous Doped crystal grown by Czochralski technique

to its effect on p-type silicon [15]. So n-type silicon is resistant to some common metals, but not all metals.

The *International Technology Roadmap for Photovoltaics* predicts n-type mono-crystalline material to reach ~10% of the total Si solar module market by the year 2015, and over 30% by 2023 [8]. This roadmap predicts a substantial shift from p-type to n-type mono-Si within the mono-Si material market [8]. Past barriers to adoption of n-type silicon cells by a broad base of cell and module suppliers include the higher cost to manufacture a p-type emitter junction and the higher cost of the n-type mono silicon crystal. Technologies to reduce the cost of manufacturing the p-type emitter by diffusion or implantation of boron are being developed in the industry [1].

Crystal growth technology defines the cost of the n-type crystal

The Czochralski (CZ) method of crystal pulling is used to economically produce large amounts of dislocation-free, single orientation ('mono') silicon for photovoltaic conversion applications. Most of this crystal is p-type, doped with boron. In the CZ method, a single crystal of silicon is grown by pulling a seed of the desired crystal orientation from the melt contained in a fused silica crucible. The CZ method is a batch process in that a crystal is pulled from a single crucible charge; the crucible is used once and is discarded after use. To increase yield per crystal growth operation and reduce unit crystal growth cost, strategies such as larger starting charge sizes or pulling several crystals sequentially from a single crucible after 'recharging' the melt with additional polysilicon, have been employed in high volume, large-scale production. However, a disadvantage of recharging the melt can be that

unwanted impurities can build up in the residual melt between recharges, due to macro-segregation. These impurities can lead to a variety of lifetime-reducing recombination centers that degrade solar cell efficiency.

The crystals are grown in the shape of right circular cylinders. To convert them to the 'pseudo-square' shape needed for solar cells, the crystals are cut from a circular to a roughly square cross section shape, and the roughly 27% mass 'wings' of the original crystal are diverted as recycle silicon for future mono crystal growing or to cast multicrystalline silicon ingots. The wings are not directly used in making the cell on the wafers sliced from the crystal. They are recycled and offset ~27% by mass the need for virgin polysilicon, contributing to lower cost of the combined polysilicon plus crystal conversion cost.

Unique challenges of n-type silicon crystal

Phosphorous is used as the n-type crystal dopant, just as it is for semiconductor device processing. During CZ crystal growth, phase diagram partition segregation of phosphorous will lead to a wide range of resistivity along the crystal length and from wafer to wafer. Figure 1 calculates and compares the resistivity distribution down the length of two CZ crystals both nominally targeted at 10 ohm-cm, one crystal p-type (boron dopant) and the other crystal n-type (phosphorous dopant). While the ratio of seed-end resistivity to tail-end resistivity for a boron doped crystal will often be slightly less than 1.8, the ratio for a phosphorous doped crystal can be 7. How detrimental this is depends on the base resistivity specification upper and lower limits for the particular device – that is, how much electrical properties are changed because of the value of base resistivity. Since there is always some error in the dopant concentration produced in the crystal – from measurement error of the dopant or polysilicon amount, variation in the crucible shape from suppliers, etc. – there is additional variation introduced from crystal to crystal. Yingli Solar reported that in high volume manufacturing, new necessary procedures had to be implemented to minimize the yield loss from resistivity non-uniformity along the length of the n-type crystals [18].

This large range of resistivity is therefore also in the 'wings' slabbed from the crystal sides as waste from making the pseudo-square shaped ingot from the crystal. If the wings possess

varying resistivity down their length, they must be carefully matched to similar resistivity sections for recycling and use in future n-type crystal growth runs; the amount of dopant to add in that run will depend on the amount of dopant already introduced in the form of recycled wings. This need to match and bin resistivity of the recycled material adds cost to the growth of n-type crystals. The n-type wings cannot be used as source poly for p-type multicrystalline ingots, or the ingots may be compensated; the n-type wings must be recycled for n-type mono growing, or roughly 27% more virgin polysilicon must be added to offset the lost wings.

Oxygen is an unavoidable chemical impurity in CZ-grown monosilicon crystals; the oxygen is introduced from dissolution of the fused silica crucible which holds the molten silicon during growth. In addition to generating LID in p-type crystal, high oxygen concentrations combined with particular but common crystal growing conditions can encourage oxygen atoms to cluster in the silicon. This leads to nano-scale microstructures, which act as charge carrier recombination centers. If oxygen concentration is high enough in the starting crystal, and cell temperatures high enough during cell manufacture on the wafers, the oxygen clusters can form with silicon a secondary silicon-oxide phase with a defined boundary, which again acts as a carrier recombination centre. Both of these types of defects would trap charges, reducing lifetime and diffusion length. Although this oxygen behavior is not unique to n-type, the recombination centres it produces can have a profound effect on the normally high lifetime n-type material, dramatically reducing the lifetime after specific cell processing steps. To preclude this, the n-type silicon may have to be grown using more complex CZ techniques, or the higher oxygen sections of crystals screened out for device use and recycled as feedstock, lowering first pass crystal yield. Both of these increase costs compared to p-type silicon grown by CZ technique.

Continuous CZ to produce n-type crystal

Continuous CZ (CCZ) can produce near-uniform resistivity mono wafers [11]. CCZ can provide quasi-steady state heat and mass transfer conditions during pulling, and produce multiple crystals during a single operation, by continuously adding polysilicon and electronic impurities during the crystal growth itself. Macroscopic crystal axial

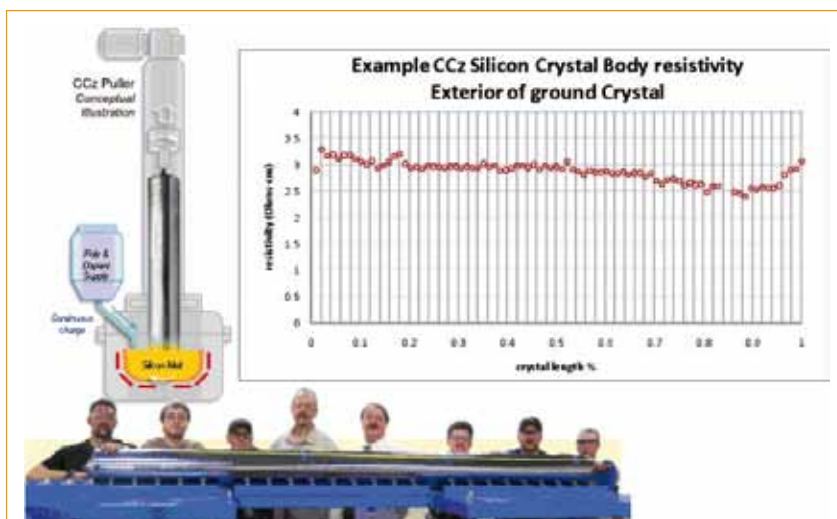


Figure 2: Crystal grown by Continuous Czochralski Technical, notional pulling process, and measured within crystal axial resistivity uniformity.

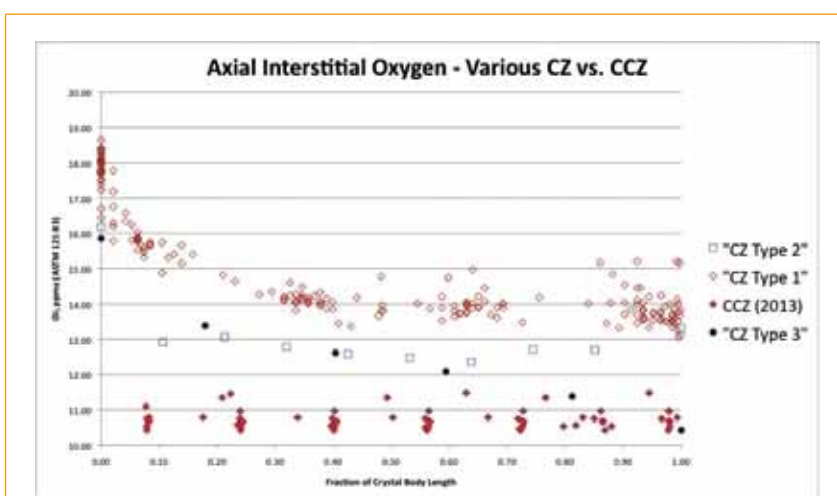


Figure 3: Measured axial crystal interstitial oxygen comparing CCZ to various CZ methods.

impurity variation is inherent in the CZ 'batch' growth process due to macro-segregation phenomena during normal freezing conditions. By continuously controlling charging of both polysilicon and dopant via CCZ, the resistivity is directly controlled.

Bulk chemical inhomogeneities in crystals grown by the conventional CZ method are a direct result of phase partitioning combined with the melt volume reduction during crystal growth. The CCZ method can be used to reduce the production cost of crystals as well as to grow crystals under quasi-steady heat and mass transport conditions, leading to quasi-uniform structural and chemical defect distributions. The CCZ process can be designed to lead to a much slower build-up of impurities than sequential melt replenishment. It has been shown that a lower impurity build-up, and greater axial uniformity of impurities incorporated, can be achieved by the CCZ method when compared to either

the conventional or sequential multiple crystal growth CZ methods [11, 12].

For more than 55 years, CCZ has been an anticipated silicon manufacturing breakthrough [10]. Research at all major silicon manufacturers (i.e., MEMC, Motorola, SEH, Siltronic, Toshiba) plus by the US government, Russia and numerous universities, did not generate a high volume manufacturing CCZ process. Several promising crystal growing configurations were generated, but were not demonstrated to have the cost or repeatability for high volume manufacturing [13,14]. However, a production-scale CCZ process has been demonstrated and is being implemented by SunEdison [11, 12]. Figure 2 shows a representative long crystal generated by the CCZ process, as well as the level resistivity along a crystal body length [11, 17]. Figure 3 shows the oxygen exhibited by CCZ process compared to representative CZ crystals grown for solar application [12].

For n-type solar cell crystal substrate, there are several benefits of the CCZ approach for n-type mono-silicon [11,12]:

1. Metered dopant/polysilicon introduction during crystal growth allows for 'uniform' axial resistivity for both p-type and n-type and improves crystal manufacturing yield (particularly for dopants with segregation coefficients $\ll 1$, such as Phosphorous). There are fewer 'bins' of solar cell power output and cell efficiency, in those cases where power or efficiency is greatly influenced by the value of base resistivity.
2. It can prevent a gradual build-up of unwanted impurities (i.e. C, metals); metals are a major determiner of lifetime.
3. The oxygen concentration can be decoupled from crucible size and crystal diameter, and relatively low oxygen concentrations obtained over long crystal lengths without use of a magnet to change the molten silicon flow conditions.
4. Many long body crystals are produced from each CCZ production run, spreading out cost per run for specialized or unusual consumables.
5. The crystal/ingot length is determined by 'height of building' (length of pull chamber) instead of crucible and hot zone and puller tank size. This allows longer crystals (and more wafers) to be made in a run without increasing the size and cost of the consumables or the production equipment.
6. The continuous supply of fresh polysilicon during body growth allows modification (shortening) of the sequential charge-melt-stabilize-grow-remove cycle for crystals.
7. Constant melt height maintains targeted bulk crystal growth conditions. The process can be designed to maximize crystal body pull speed for higher crystal productivity.
8. Quasi steady-state distribution of bulk micro-defects in the crystal can be realized from the quasi steady growing conditions. The majority of crystal length can be cooled under similar conditions, which should lead to similar grown-in micro-defects in wafers produced from each crystal.

Conclusion

It is likely that solar cell architectures will migrate from 'traditional' p-type Al back-surface field (BSF) cells to more advanced p-type cells and ultimately to n-type cells, due to cost/watt-peak reductions needed for modules and the independent impact on balance-of-systems economics. This increased efficiency should be particularly beneficial to residential installations. One barrier to adoption of n-type high efficiency cells is the cost of n-type mono crystal. CCZ is being developed or implemented by several companies to enable a large supply of n-type Si for high efficiency Si cells. This will allow avoidance of crystal yield loss from both resistivity extremes due to axial phosphorous segregation as well as high oxygen concentration. It will also potentially reduce the number cell bins, when that binning is influenced by the base resistivity. CCZ can enable more uniform material properties and reduced wafer costs.

There are several different technical approaches to CCZ being implemented by different equipment makers and wafer suppliers. The specific CCZ technical approach will determine if productivity is high and conversion cost is low enough to be implemented for solar PV applications, but it is likely that at least one approach will be successful.

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