

Crystal Growth and Materials Research in Photovoltaics: Progress and Challenges

R.SARATHA M.Sc., M.Phil., B.Ed.,

Abstract

Photovoltaics (PV) is *solar electric power*—a semiconductor-based technology that converts sunlight to electricity. Three decades of research has led to the discovery of new materials and devices and new processing techniques for low-cost manufacturing. This has resulted in improved sunlight-to-electricity conversion efficiencies, improved outdoor reliability, and lower module and system costs. The manufacture and sale of PV has grown into a \$5 billion industry worldwide, with more than 740 megawatts of PV modules shipped in 2003. This paper reviews the significant progress that has occurred in PV materials and devices research over the past 30 years, focusing on the advances in crystal growth and materials research, and examines the challenges to reaching the ultimate potential of current-generation (crystalline silicon), next-generation (thin films and concentrators), and future-generation PV technologies. The latter includes innovative materials and device concepts that hold the promise of significantly higher conversion efficiencies and/or much lower costs.

Introduction

The traditional concept of photovoltaics (PV) or solar cells is that of a solid-state device that produces useful electricity (direct current and voltage) from the Sun's energy via the photovoltaic effect. When sunlight strikes the cell, the part of the solar spectrum with energy above the bandgap of the semiconductor material imparts enough energy to create electron–hole pairs. A junction formed between dissimilarly doped semiconductor layers sets up a potential barrier in the cell, which separates the light-generated carriers. This induces a fixed electric current (dependent on cell area) and a voltage (dependent on the nature of the doped layers) in the device. The electricity is collected and transported by metallic contacts on the top and bottom surfaces of the cell.

Historical trends of success

More than 30 years of worldwide research on terrestrial PV has resulted in significant advances in research and the markets, as well as in significant cost reductions for PV systems and improvements in the reliability of all system components. One of the most significant trends is the continuous improvement of solar cell efficiencies for all technologies. A number of these, specifically thin films and multijunction concentrator cells, owe their genesis to the terrestrial PV research

PV technology options

Photovoltaic technologies can be divided into two main areas: flat plates and concentrators. Flat-plate technologies include crystalline silicon (from both ingot and ribbon- or sheet-growth techniques) and thin



films of various materials, usually deposited on some low-cost substrate, such as glass, plastic, or stainless steel, using some type of vapor deposition, electrodeposition, or wet-chemical process. Thin-film cells typically require one-tenth to one-hundredth of the expensive

Emerging silicon crystallization technologies

Several low-cost growth technologies have been or are in various stages of development. Emerging technologies namely Mono-like Silicon, NOC-Si and KE-Si are of particular interest, due to recent achievements in material quality improvement. Mono-like Silicon technology has already been introduced into the PV market and had ~2% share in 2015 large-diameter ingots (up to 90% of the crucible diameter) and efficiencies comparable to those of CZ wafers have recently been reported for NOC-Si and high efficiency large area (>243 cm²) silicon heterojunction (SHJ) solar cells with up to 23% efficiency has recently been reported for KE-Si . Despite the impressive achievements in these emerging technologies, many challenges including inhomogeneity in material properties still remain.

Mono-like Silicon

Crystallization of mono-like or Quasi-monocrystalline ingot uses standard mc-Si crystallization equipment and is therefore a low-cost technology. In this growth method, mono-Si blocks are used as seeds as shown in **Fig. 1**. The feedstock with dopants is melt and the seeds are partially melted, so that during crystallization, the growing crystal adopts the orientation of the seed. However, due to crucible-side grain nucleation, the ingot is only partly monocrystalline. The monocrystalline part of the material can be of high quality, with minority carrier lifetimes and diffusion lengths suitable for high efficiency solar cells. Large area (103.9 cm²) n-type mono-like SHJ solar cell with efficiency > 21.5 % has been reported.



Fig. 1. Mono-like silicon ingot growth

The potential of the mono-like silicon growth method as a low-cost high-quality PV silicon material is large. However, the technology faces many challenges that prevent its maturity. shows estimated



contribution of cast silicon material to crystalline silicon market share for 2020 as forecast by International Technology Roadmap for Photovoltaic (ITRPV). The technology was once projected to dominate the PV market, replacing standard multicrystalline silicon. However, due to lack of maturity and introduction of HPMS material, the contribution of mono-like silicon in the PV market is expected to remain below 2%.

Mono-like silicon material suffers from many of the standard multicrystalline silicon problems, including structural defect generation and multiplication. Seed junction and crystal junctions are important sources of dislocations . Unlike in mc-Si silicon where dislocations may be terminated at grain boundaries, dislocations in mono-like Si can easily propagate and multiply to form clusters of high dislocation density. Grain nucleation from crucible-wall and seed joints results in parasitic multicrystalline silicon, which may exceed 50% of the ingot for standard mono-like silicon growth . This poses serious challenges in wafering and texturing processes due to non-uniformity of the material properties. Furthermore, seeds and difficulties in seed recyclability add to the cost/Wp.

Non-Contact Crucible Silicon

Crucible is a major source of impurities and structural defects in cast PV-Si, including standard mc-Si, HPMS and mono-like Si. One technique to reduce the impact of the crucible is to use Kyropoulos or similar growth method, to reduce contact between the crucible and solidified silicon during crystallization. Kyropoulos growth method, is widely used for growing large unconfined (stress-free) single crystals of alkali halides from the melt . Although the Kyropoulos method is more than 75 years old, the technique did not attract much attention for use in crystallization of silicon. The method was demonstrated to grow silicon single crystals for the first time in 1985. Recently, there has been a renewed research interest for using similar methods for production of high quality PV-silicon wafers at low cost. In this section, we review some of the progress and challenges in the Floating Cast or the Non-Contact Crucible Silicon (NOC-Si)





NOC-Si employs cast method to grow silicon ingots inside the melt, i.e., unconfined by the crucible walls during crystallization. In this growth method, (**Fig. 2**), the feedstock is melt in a crucible, followed by nucleation at the top center of the melt, which is either by local cooling, or by seeding as in CZ-Si growth method. Theingot is then crystallized by pulling and/or controlled temperature distribution of the furnace such that the growing crystal does not come into contact with the crucible wall during the course of crystallization, reducing stress, in- diffusion of impurities from the crucible and grain nucleation from the crucible walls. High-quality large-diameter (up to 90% of the crucible diameter) has been demonstrated . Owing to the minimization of stress and in- diffusion of impurities from the crucible, a low dislocation density of < 10^3 cm⁻², impurity contamination near or below the detection limit of ICP-MS and synchrotron-based μ -XRF, minority carrier lifetimes >3.2 milliseconds and solar cell efficiency of up to 19.6%, has been achieved.

Along with the cost, which is expected to be higher than the cost of mc-Si materials, several material related challenges must be adequately addressed for the NOC-Si growth method. Firstly, low as-grown lifetimes, necessitates gettering for achievement of full potential of the material. As-grown lifetime is suspected to suffer from contamination by fast diffusing impurities from sources such as furnace parts and growth environment. Stringent impurity control such as cleaning the growth environment between growth runs and shielding the furnace area required, or implementation of ingot annealing and cooling regimes for point defect precipitation or out- diffusion may be required. Secondly, swirl-like defects, similar to point defect patterns in CZ-Si, causing lateral and vertical inhomogeneity in material properties along the ingot height, must be minimized. shows effective minority carrier lifetime measured by Quasi-Steady-State Photoconductance (QSSPC) at 1×10^{15} cm⁻³ injection level on NOC-Si wafers, subjected to standard and extended gettering schemes reported in Ref. [22]. The wafers came from the same block of the ingot. Lateral positions (LP1, 2 etc) refers to 5cm x 5cm wafers cut from the same originally 15.6cm x 15.6cm wafer. It is observed that lifetime and gettering efficiency deteriorates significantly for the ingot-middle and bottom wafers due to presence of swirl-like defects. Inhomogeneity in gettered lifetime within wafer is also evident

Summary and Conclusions

In this contribution, we have reviewed progress and challenges in emerging technologies for crystallization of photovoltaic silicon. Significant progress in both material quality and throughput has recently been achieved in Mono-like silicon, Non-contact crucible silicon and Kerfless Epitaxial silicon growth methods. Challenges, especially presence of structural defects and parasitic mc-Si causing non-uniformity in material properties appears to be a limiting factor for sluggish commercial share of mono-like silicon. 19.6% and 23% solar cell efficiencies have been reported for Non-contact crucible silicon and Kerfless Epitaxial silicon respectively, in high efficiency SHJ solar cell architecture. Presence of swirl-like defects, as-grown lifetime-limiting defects and non-uniformity in materials property must be adequately addressed. In general, there is great potential for Mono-like silicon, Non- contact crucible silicon and Kerfless Epitaxial silicon for use in high efficiency low-cost solar cells.



References

- International Technology Roadmap for Photovoltaic (ITRPV) 2017. Seventh Edition; Results 2016; http://www.itrpv.net/Reports/Downloads/
- 2. Luque A, Hegedus S. (Eds). Handbook of photovoltaic science and engineering: John Wiley & Sons 2011.
- 3. Powell DM, Winkler MT, Goodrich A, Buonassisi T. Modeling the Cost and Minimum Sustainable Price of Crystalline Silicon Photovoltaic Manufacturing in the United States. IEEE Journal of Photovoltaics 2013; 3:662-668.
- 4. Ryningen B, Stokkan G, Kivambe M, Ervik T, Lohne O. Growth of dislocation clusters during directional solidification of multicrystalline silicon ingots. Acta Materialia 2011; 59:7703-7710.
- 5. International Technology Roadmap for Photovoltaic (ITRPV) 2016. Seventh Edition; Results 2015 including maturity report; http://www.itrpv.net/Reports/Downloads/
- 6. Nakajima K, Ono S, Murai R, Kaneko Y. Growth of Si Bulk Crystals with Large Diameter Ratio Using Small Crucibles by Creating a Large Low-Temperature Region Inside a Si Melt Contained in an NOC Furnace Developed Using Two Zone Heaters. Journal of Electronic Materials 2016; 45:2837-2846.
- 7. Jensen MA, LaSalvia V, Morishige AE, Nakajima K, Veschetti Y, Jay F, Jouini A, Youssef A, Stradins P, Buonassisi T. Solar Cell Efficiency and High Temperature Processing of n-type Silicon Grown by the Noncontact Crucible Method. Energy Procedia 2016; 92: 815-821.
- 8. Kobayashi E, Watabe Y, Hao R, Ravi TS. Heterojunction solar cells with 23% efficiency on n-type epitaxial kerfless in Photovoltaics: Research and Applications 2016; 24:1295-1303.
- Bliss DF. Evolution and application of the Kyropoulos crystal growth method. In: 50 years Progress in Crystal Growth, A reprint collection. R. S. Feigelson, Ed. Amsterdam, The Netherlands: ELSEVIER B.V; 2004;50: 29-33.
- 10. Ravishankar PS. Kyropolous crystal growth of silicon for solar cell applications 1985. Solar Energy Materials 1985;12:361-369.
- ^{11.} Nose Y, Takahashi I, Pan W, Usami N, Fujiwara K, Nakajima K. Floating cast method to realize high-quality Si bulk multicrystals for solar cells. Journal of Crystal Growth 2009; 311:228-231.
- 12. Nakajima K, Morishita K, Murai R, Kutsukake K. Growth of high-quality multicrystalline Si ingots using noncontact crucible method. Journal of Crystal Growth 2012; 355:38-45.
- 13. Nakajima K, Murai R, Morishita K, Kutsukake K, Usami N. Growth of multicrystalline Si ingots using noncontact crucible method for reduction of stress. Journal of Crystal Growth 2012; 344:6-11.
- 14. Kivambe M, Powell DM, Castellanos S, Jensen MA, Morishige AE, Nakajima K, Morishita K, Murai R, Buonassisi T. Minority-carrier lifetime and defect content of n-type silicon grown by the noncontact crucible method. Journal of Crystal Growth 2014; 407; 31-36.
- Castellanos S, Kivambe M, Jensen MA, Powell DM, Nakajima K, Morishita K, Murai R, Buonassisi T. Exceeding 3 ms Minority Carrier Lifetime in n–type Non-contact Crucible Silicon Energy Procedia 2016; 92:779-784.