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Crystalline-Silicon Solar Cells for the 21^{st} Century

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CRYSTALLINE-SILICON SOLAR CELLS FOR THE 21ST CENTURY

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ABSTRACT

The worldwide market share for crystalline-silicon solar cells has increased steadily in the last 10 years. In 1998, about 87% of the photovoltaic modules shipped worldwide are based on crystalline silicon. This dominance will likely continue into at least the first few years of the 21st century. The long-term growth of crystalline-silicon solar cells will depend on the development of low-cost polysilicon feedstock, silicon films, and advanced cell and module manufacturing processes.

INTRODUCTION

The worldwide photovoltaic (PV) module shipments for terrestrial applications reached 152 MW/year in 1998. Crystalline-silicon (c-Si) solar cells currently account for about 87% of the worldwide PV module shipment (Fig. 1 and Table I).

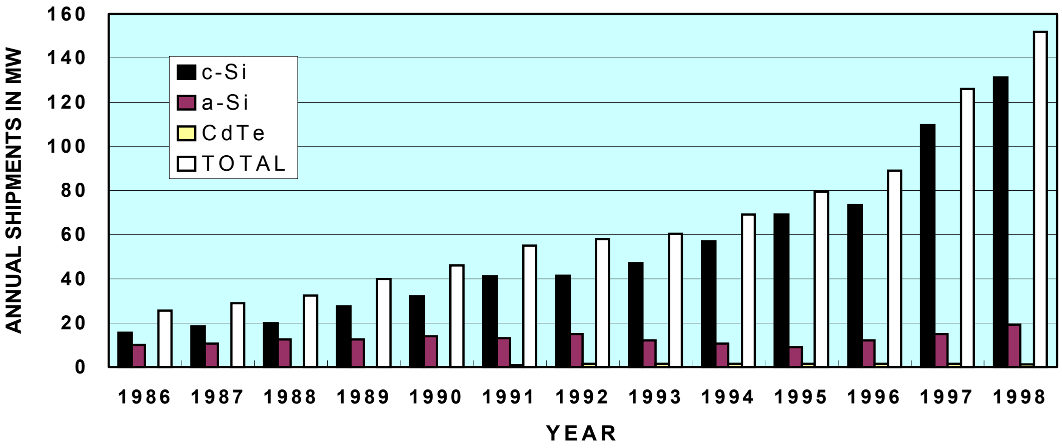

Figure 1. Worldwide PV shipments (in MW) by material technology.
(Main source of data: *PV News*, Paul D. Maycock, editor)

Table I. Overall market share for c-Si PV modules from 1990 to 1998
(including single-crystal, polycrystalline, ribbon, and concentrator Si)

	1990	1991	1992	1993	1994	1995	1996	1997	1998
World (%)	67.7	73.8	72.7	77.3	81.3	82.1	82.9	83.3	86.5
U.S. (%)	90	95	93	96	96	96	96	94	93

There are many reasons for the dominance of c-Si in PV: stable performance, low module manufacturing cost (presently less than $\$2.5/W_{peak}$), and mostly non-toxic materials used in the final product. There are four types of c-Si solar cells: single-crystal, polycrystalline, ribbon, and silicon film deposited on low-cost substrates. In 1998, market shares of the worldwide PV cell and module shipment for the four types of crystalline-silicon solar cells were 39.4% for single-crystal, 43.7% for polycrystalline, 2.6% for ribbon, and 0.7% for silicon film (1). This is the first time ever that polycrystalline silicon has overtaken single-crystal silicon as the PV market leader.

We believe that to ensure the continued growth of the c-Si PV industry in the next century, three research and development areas (2,3) need to be extensively investigated in the near future: (1) innovative approaches for producing low-cost polysilicon feedstock, (2) low-temperature, high-throughput, thin-layer silicon deposition methods, and (3) environmentally benign cell and module manufacturing processes. In this paper, we will identify the main issues that need to be addressed for each of these activities.

LOW-COST POLYSILICON FEEDSTOCK

For crystal-growth feedstock, the c-Si PV industry has been relying on waste material from the semiconductor Si industry and on *secondary polysilicon*, the excess or rejected material from electronic-grade polysilicon production. This amounts to about 10% of the polysilicon material used by the semiconductor Si industry. If the PV industry continues to grow at the present rate, which in recent years has been higher than the growth rate of the integrated-circuit industry, new sources of polysilicon will be needed (4,5). New approaches need to be investigated for producing solar-grade polysilicon at costs of less than US$10/kg. The purity requirements for solar-grade polysilicon, according to the Solar-Grade Silicon Stakeholders Group, are the following: it is preferred that polysilicon have either B or P doping, with no compensation; resistivity at $25^{o}C$ should be greater than 1 ohm-cm; oxygen and carbon should not exceed the saturation limits in the melt; and the total non-dopant impurity concentration should be less than 1 ppma (6).

More than 98% of semiconductor-grade polysilicon is produced by the trichlorosilane ($SiHCl_3$) distillation and reduction method (7). This method of polysilicon production is very energy intensive, and it produces large amounts of wastes, including a mix of environmentally damaging chlorinated compounds (8). About 80% of the initial metallurgical-grade silicon (MG-Si) material is wasted during the process. In addition, the semiconductor-grade polysilicon material produced by this method far exceeds the purity requirement of the PV industry, and the cost (over US$50/kg, with most of it attributable to the $SiHCl_3$ processes) is several times higher than what the PV industry can afford. Recently, several programs have been initiated to investigate less energy-intensive and chlorine-free methods of producing solar-grade polysilicon. Examples include a method that uses MG-Si and absolute alcohol as the starting materials (2), a method of producing solar-grade polysilicon by directly purifying MG-Si pellets using porous silicon etching and subsequent annealing (9), and a method of using an electron-beam furnace and a plasma furnace to remove impurities from MG-Si (10).

SILICON FILMS

Thin-Layer Polycrystalline Silicon

Thin-layer c-Si solar cells have great potential for low cost, high efficiency, low material consumption, long-term stability, and environmental friendliness. The challenge in developing this technology is in fabricating an active silicon layer of sufficient electronic quality, with a thickness of 10 microns or more, at a deposition rate of over 1 micron/min, and on a low-cost substrate such as glass. The principal requirement on electronic quality is a long minority-carrier diffusion length that is at least comparable to the layer thickness.

Liquid-phase epitaxy (LPE) growth methods have been extensively studied to produce thin silicon layers on low-cost MG-Si silicon substrates (11). One of the more successful methods, which uses Cu-Al solvents for LPE growth of silicon, provides higher growth rates (~1 micron/min) and better nucleation than commonly used indium solvent and yet suppresses Cu and Al incorporation in the layer better than Cu or Al alone (12). The crystal perfection achieved by LPE is inherently better than gas-phase growth techniques because of the near-equilibrium growth process. However, this also limits the substrate choice to silicon because the free-energy driving force in LPE is usually not enough for nucleation on foreign substrates without incurring simultaneous nucleation in the liquid.

Gas-phase growth techniques can deposit large-grain polycrystalline thin-layer silicon on a foreign substrate at a high rate with minimum contamination. The technique needs to provide enough driving force for heterogeneous nucleation and reduced number of nucleation sites. Alternately, a seeding silicon layer on a foreign substrate may be used. However, conventional chemical-vapor deposition (CVD) methods have had only limited success in depositing thin-layer silicon for PV applications. For example, thermal CVD requires too high a substrate temperature (13), and plasma-enhanced CVD (PECVD) has too slow a deposition rate for low-cost thin-layer polycrystalline silicon (14). Post-deposition solid-phase crystallization can be a way of avoiding the aforementioned limitations of deposition methods (15). However, the disadvantages of solid-phase crystallization include low throughputs and the tendency to induce stress in the films. Alternatively, advanced light-trapping techniques can reduce the thickness requirement for thin-film silicon solar cells and make it feasible to use low-deposition-rate methods. For example, a PECVD-deposited, 2-micron-thick polycrystalline silicon solar cell with light trapping was shown to have a conversion efficiency of more than 10% (16).

Atmospheric pressure and rapid thermal CVD (AP-RT-CVD) seems to be a promising method to achieve fast deposition of polycrystalline silicon layers on foreign substrates (17). However, to achieve adequate grain sizes, the depositions had to be done at elevated substrate temperatures. This speeds up impurity contamination and limits substrate selections. The challenge is to find a growth method that has a driving force between that of the LPE and the AP-RT-CVD techniques to facilitate sparse nucleation on foreign substrates for fast deposition of large-grain silicon layers at relatively low temperatures.

Microcrystalline Silicon

Microcrystalline (or nanocrystalline) silicon films produced by plasma-enhanced chemical-vapor deposition (PECVD) through a glow discharge containing silane diluted in argon, helium, and/or hydrogen have optical and electrical properties different from hydrogenated amorphous silicon and conventional polycrystalline silicon (18). These microcrystalline silicon films are often a mixture of hydrogenated amorphous silicon and polycrystalline silicon grains, with grain size from a few nanometers to a few hundred nanometers. These films can exhibit optical properties characteristic of a direct bandgap material (19). They have higher electrical conductivity and mobility than hydrogenated amorphous silicon. Microcrystalline silicon films are widely used as contact layers and tunnel junctions in amorphous silicon and multiple-junction solar cells. A solar cell using microcrystalline silicon as the active layer was reported with a high initial efficiency of 13.1% (20, 21). Plasma deposition methods and low deposition temperatures make it easy for depositing microcrystalline silicon solar cells on low-cost substrates over large areas. However, low deposition rates and light-induced degradation are concerns for microcrystalline solar cells.

Porous Silicon

It was discovered in 1990 that porous silicon formed on crystalline-silicon wafers using electrochemical etching exhibits photoluminescent and electroluminescent properties similar to those properties of a semiconductor with a direct energy gap (22). Porous silicon layers can be easily produced on single- or multicrystalline silicon surfaces by electrochemical or stain etching at very low cost. Several possible methods of using porous silicon to improve the performance of crystalline silicon solar cells have been proposed since then. It was shown that a porous silicon-etched silicon surface has excellent anti-reflection properties (23). Porous silicon may also serve as a wide bandgap absorber in a multiple-junction cell structure, with crystalline silicon as the substrate or as gettering centers to reduce the impurity levels in a silicon substrate (24). A porous-silicon back-surface reflector has been demonstrated for thin-film silicon solar cells (25). Attempts were even made to use two porous silicon layers with two different bandgaps in a three-bandgap solar cell on a silicon wafer (26). Although porous silicon has not yet been used in any commercial silicon solar cell yet, it remains a potential resource for improving the crystalline-silicon solar cell technology.

ADVANCED CELL AND MODULE MANUFACTURING PROCESSES

Environmentally Benign Manufacturing Processes

The manufacturing of c-Si solar modules -- from polysilicon production, to crystal growth, ingot slicing, wafer cleaning, cell processing, and encapsulation -- requires many steps that are energy intensive and uses large amounts of water and toxic chemicals. As the c-Si PV industry continues to expand, the environmental impact of its manufacturing processes and products will receive increasing attention, because one of the primary benefits of renewable-energy generation is its low environmental impact. Examples of new and more environmentally benign approaches for manufacturing silicon cells and modules include (2):

- Automated processes for handling thin (< 200-micron-thick) silicon wafers (27),
- Defect passivation methods to improve cell conversion efficiency (28),
- Water-soluble or water-based slurries for multiple-wire saws and slurry recycling,
- Reduction, recovery, recycle, reuse, and substitution for water and chemical usage for wafer cleaning and etching,
- Reducing or eliminating the use of perfluorinated compounds for cell processing,
- No-clean flux, and
- Lead-free solder.

Environmentally benign manufacturing approaches often have the added benefit of cost reduction by reducing energy use and/or the purchase volume of new chemicals and by cutting the amount of spent chemicals that must be discarded. A good example of a new, more environmentally benign approach that also improves module performance is the Sn(96.5)/Ag(3.5) lead-free solder. A recent report (29) shows that this solder has better thermal performance characteristics over the industry standard Sn(60)/Pb(40) solder in commercially available photovoltaic modules.

Rapid Thermal Processing

Rapid thermal processing (RTP, 30) has some important advantages over traditional furnace processing, including shorter process times, lower thermal budgets, lower chamber wall temperatures, and better control over ambient conditions due to reduced reactor volume (31). Possible applications of RTP in crystalline-silicon solar cell processing include junction formation (32), selective doping (33), thermal oxidation, and drying and firing of screen-printed metal pastes. Concentrated light may also be used for solid-phase crystallization of thin-film silicon (34). However, the high cost and low throughput of single-wafer RTP systems limit the use of RTP's application in PV solar cell manufacturing. Multiple-wafer RTP systems have become commercially available recently. However, the cost of such systems is still too high compared to traditional furnaces. In addition to the thermal effects, photons with energy near or above the bandgap energy may also have beneficial effects (35, 36). However, more studies are needed to more clearly demonstrate these benefits.

CONCLUSIONS AND DISCUSSION

With increasing automation and economy of scale, the present generation of crystalline-silicon solar cells, including single-crystal wafers, polycrystalline wafers, ribbons, and sheets will continue to dominate the photovoltaic solar cell market for at least the first ten years of the 21st century. The substrate areal throughputs for the leading growth processes are in the range 5-20 m^2/h per growth station, and matching process line rates are in place. A near-term goal of 100 m^2/h is actively pursued for some of the growth methods. The long-term growth of the crystalline-silicon solar cell industry depends on the development of low-cost polysilicon feedstock (for further expansion of the current growth methods) and on c-Si thin-layer growth or thin films for processes that minimize material consumption and accommodate monolithic processing. Candidates for such approaches include thin-layer polycrystalline silicon, microcrystalline-silicon thin films, and porous-silicon thin films. For such processes to be viable, they must be capable of matching the throughputs of existing approaches. As the size of the Si PV industry continues to increase, environmental impact of the manufacturing procedures will be a growing concern, and processes that mitigate the impact will be essential.

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