JPL Quarterly Technical Review Volume 2, Number 4 January 1973

Index: environmental sciences, industrial processes and equipment, power sources

Development of a Thick-Film Silicon Ribbon Growth Technique for Application to Large-Area Solar Cells and Arrays

P. A. Berman

Guidance and Control Division

A new technique is described for growth of large-area silicon ribbons. This technique is an edge-defined, film-fed growth process by which single crystals can be grown having a shape controlled by the *outside* dimensions of a shaping die, growth taking place from an extremely thin film of liquid fed by capillary action from a crucible below. The material from which the die is fabricated is very critical to the process. The die must be wet by the silicon, but adverse impurities must not be introduced into the silicon, and the die must not become degraded by the molten silicon. A breakthrough in die fabrication that has allowed the growth of silicon ribbons having dimensions of 1 cm by 30 cm with a thickness of 0.7 mm is described. The implications of this significant advancement with respect to development of photovoltaic solar arrays for wide-scale terrestrial solar-to-electric energy conversion systems are discussed.

Introduction

The phenomenal growth of electrical power consumption has been well documented as has the environmental impact associated with satisfying these growth requirements. Public concern is being expressed in increasingly intense terms with respect not only to the obvious pollution caused by fossil-fuel-burning electrical power generators, but also to electrical power generation by nuclear reactor systems because of their inherent problems in safety, waste disposal, fuel, and thermal pollution. Solar photovoltaics, on the other hand, represents a very benign method of electrical power generation because the conversion process is totally nonpolluting, has no moving parts, does not consume fuel of any kind, and does not require heat (in fact, heat decreases the conversion efficiency). Photovoltaic solar arrays, which have successfully operated in the environment of space to provide electrical power for almost all unmanned spacecraft, are at the present time far too expensive for wide-scale use for terrestrial electrical power generation. This is primarily due to the high costs of ultrapure, single-crystal silicon, of processing of the silicon into photovoltaic converters, and of fabrication of the photovoltaic converters into solar arrays (Refs. 1 and 2). For solar photovoltaic arrays to become economically feasible producers of electrical energy for wide-scale terrestrial use, these costs must be reduced by a factor of about one thousand over those costs presently experienced in the space program. It appears that significant progress towards these ends can be achieved through development of a thick-film silicon ribbon growth process for reasons outlined below.

Background

Silicon is the material from which space-type photovoltaic devices (solar cells) are fabricated because it is the most well understood semiconductor material from a device viewpoint (due to the research and development funded primarily by the semiconductor industry), and because it is capable of yielding solar cells having reasonable conversion efficiency (11 to 13%) and stability. Furthermore, it is a readily available semiconducting material, and although costly on an absolute basis, it is presently still the most economical material for photovoltaic converters on a dollar-per-watt basis.

To be economically attractive for wide-scale electrical power generation, however, solar cell costs must be decreased by approximately three orders of magnitude. A significant portion of these cell costs are associated with the use of ultrapure, single-crystal silicon, which presently costs on the order of $.30 per gram (Refs. 2 and 3), and which, in ingot form, the only configuration presently available, results in wastage of greater than 75% of the silicon by the time it is cut into rectangular blanks having a thickness of approximately 0.3 mm. Moreover, with respect to solar cell and array fabrication, a considerable fraction of the cost is involved in processing, handling, interconnecting, and attachment of large numbers of relatively small (the most common size having a 4 cm^2 area) solar cells and solar cell blanks (Refs. 1 and 2).

The use of large-area cells presents an overall cost advantage in array fabrication if the cells on a unit-area basis are no more expensive than the small-area cells. This is because the cell laydown and interconnection of fewer numbers of large-area cells should be significantly less expensive than for similar operations performed on a greater number of small-area cells. Similarly, the use of large-area blanks should result in a cost advantage in cell fabrication, with appropriate process modifications, because fewer pieces must be handled to fabricate a given total cell area (i.e., power generating capacity).

Large-area cells can be achieved by cutting the silicon ingot into large disc-shaped blanks (Refs. 4 and 5), rather than rectangular blanks as is presently the case, thus making use of the natural cylindrical geometry of the ingot, which can be grown with diameters as large as 7.5 cm. These cells, however, have a poor panel packing factor compared with rectangular cells and thus the power density of the array is compromised. Large rectangular cells can be obtained by a second method, namely by slicing the ingot so that the major axis of the rectangle is parallel to the ingot growth axis, thus making use of the length of the ingot rather than the width (which is of smaller dimension). This latter method, however, necessitates a tradeoff between the maximum size of the blank as against ingot utilization due to the geometric constraints involved in cutting rectangles from cylinders.

One of the major systems proposed for large-scale solar photovoltaic energy converters is a Satellite Solar Power Station (SSPS) (Refs. 6 and 7), a large central electrical power generating station located in synchronous orbit, which, even using silicon cells having a thickness of 0.05 mm as contrasted with Mariner-type solar cells having a thickness of 0.4 mm, has a proposed system weight of 18- to 45-million kg (40- to 100-million lb). Slicing the silicon ingot to provide blanks of 0.05-mm thickness will result in even greater silicon wastage due to the increased number of saw cuts and lapping required per ingot (i.e., while the number of blanks per ingot is increased, the number of saw cuts is proportionally increased. Moreover, each blank must be lapped and etched, similar to thicker cells, so that the total silicon wastage per ingot is greater for 0.05-mm thick blanks than for 0.4-mm blanks). With respect to the cutting of thin silicon cell blanks, there must be a compromise between the maximum-area dimensions and the minimum-thickness dimension due to breakage factors associated with the relatively brittle silicon material. Hence it appears that ultrathin 0.05-mm-thick cells will be difficult to achieve for areas much greater than the commonly used 4 cm^2, if one is constrained to cut the blanks from an ingot as is presently done.

In addition, over and above the material wastage and breakage problems, the cutting operations induce defects in the silicon, which are to some extent removed by lapping and etching, but which still remain significant, adversely affecting the resultant cell performance.

Motivated by the need for large-area, highly efficient, lightweight (i.e., thin) solar cells, the Jet Propulsion Laboratory solicited proposals from industry pertaining to the development of thick-film silicon growth techniques. The effort as delineated by the JPL Statement of Work was to be directed toward a program "to develop a technique for producing P-type silicon films of quality, thickness, and area requisite to the production of low-cost, high-efficiency (sic), large-area solar cells." Thus the goal would be a process whereby silicon can be grown in the form of a large or continuous area "blank," requiring no lapping, sawing, or etching, making maximum use of the silicon material, and allowing the fabrication of very-large-area, thin solar cells. The effort defined by the JPL Statement of Work includes determination of process control requirements (e.g., thermal, mechanical, and operator control requirements, as well as in-process evaluation requirements), determination of maximum-area dimension capability, determination of film-thickness capability, determination and optimization of film dimensions, determination and optimization of consistency of film crystalline properties (such as resistivity, dislocation density, and impurity density), determination and optimization of film growth, determination of stability of equipment used in processes, determination of in-process replenishment requirements of silicon and dopants, submission of 20 sample state-of-the-art silicon films having an area of 1 cm by 2 cm and a thickness of 0.1 mm, and submission of 10 sample state-of-the-art silicon films having an area of 20 cm^2 and a thickness of 0.1 mm.

On the basis of the responses received, JPL selected Tyco Laboratories, Inc. to perform this effort under JPL Contract No. 953365 (initiated February 1972) using the Edge-Defined Film Growth (EFG) process developed by Tyco for growth of sapphire ribbons, filaments, and tubes.

Description of the EFG Process

Edge Defined Film Growth is a process by which single crystals can be grown having a shape controlled by the *outside* dimensions of a die, growth taking place from an extremely thin film of liquid fed by capillary action from a crucible below (Ref. 8). This method appears to be more stable than other methods of shaped growth and shows great promise for being an industrially feasible process for the formation of single-crystal silicon ribbon directly and continuously from the melt.

A quartz crucible is used to contain silicon heated above the silicon melt point. The bottom surface of the die is immersed into the molten silicon such that the molten silicon is able to enter capillary slots or tubes located within the die; these slots are perpendicular to the top and bottom die faces. If the contact angle between the molten silicon and the die material is less than 90°, and the geometry of the capillary slots or tubes is properly designed, the molten silicon rises by capillary action to the upper surface of the die. The contact angle Θ is defined as the angle between the tangent of the molten silicon at the point of contact to the die material and the surface of the die at point of contact; that is to say, complete wetting corresponds to $\Theta = 0°$ and no wetting whatsoever corresponds to $\Theta = 180°$. A small diameter silicon seed having the desired crystallographic orientation is inserted into the capillary seed slot in the upper face of the die and the temperature adjusted so that the silicon solidifies onto it. By proper control of temperature and seed withdrawal rate, the molten silicon begins to spread across the die surface until it reaches the edges of the die, at which point the liquid spreading is halted because of the 90° change in effective contact angle at the outer perimeter. With proper adjustment of temperature and pull rate, the crystal will then continue to grow with a cross-sectional area and shape determined by the outside perimeter of the die. The physics of this process are such that it is self-stabilizing over a relatively wide range of power input fluctuations by means of changes in the thickness of molten film. Furthermore, the growth interface is effectively decoupled from the bulk melt surface, permitting continuous replenishment of the melt during growth. This is of great importance in establishing a low-cost process with maximum equipment utilization since the machine does not have to be shut down to replace the silicon charge and this is a considerable advantage of the EFG process over other methods of silicon growth. Another distinct advantage is to be found with respect to consistency of chemical composition (i.e., impurity distribution). Because of the fast growth rate and the faster linear motion rate of the liquid supply, segregation effects are negligible and hence the solidified silicon crystal has the same chemical composition as the bulk liquid.

In the past, a significant research effort was expended by the Air Force on a webbed dendrite technique of ribbon growth, but the technique was not found to be economically feasible because of the very stringent controls required. For example, it was found necessary to maintain growth temperatures constant to within ±0.02°C, which not only imposed excruciatingly difficult control requirements but also rendered crucible replenishment practically impossible.

Because of the inherent characteristics of the EFG process, such stringent controls are not required. EFG-grown sapphire ribbon is routinely grown with minimum operator control at the Tyco facility. The contractor is commercially producing sapphire ribbons, cylindrical rods, and other complex shapes using the EFG technique.

The major problems to be overcome in the growth of silicon ribbons by the EFG technique are associated with the growth-die: specifically, the geometry of the die and the material from which the die is made. The die must be wet by the silicon, but adverse impurities must not be introduced into the silicon, and the die must not become degraded by the molten silicon. Because of the reactivity of silicon at growth temperatures (about 1400°C), these conditions are not easily satisfied; however, a significant number of options exist (Refs. 9 and 10).

The major advantages of the EFG technique are: production of accurately controlled cross sections, self-stabilization over relatively wide ranges of power input fluctuation by means of changes in the thickness in the molten film, growth rates limited only by latent heat removal from the solid-liquid interface, decoupling of the growth interface from the bulk melt surface permitting continuous replenishment of the melt during growth, arbitrary choice of crystalline orientation, minimization of segregation effects due to the fast growth rate and linear motion rate of the liquid supply, and high crystalline perfection.

Status of the Program

A number of techniques for fabricating the growth die are being investigated (Refs. 9 and 10). Dies made of the following materials are being evaluated: silicon carbide obtained by conversion of high purity graphite (for example Dow Corning Pyrobond), quartz-silicon combinations, quartz-silicon carbide combinations, graphite, and beryllium oxide. In conjunction with this, studies on the die configuration (geometry) are also being made along with methods of temperature control across the die surface. Thus, the approach is to investigate various materials as well as configuration of the die and methods of temperature control, including heat shielding, in an attempt to mitigate the degradation of die materials. With respect to die configuration and temperature control, it appears advantageous to have the ends of the orifice receive less heat than the middle, and the configuration and shielding modifications are being made to achieve this end. A very brief description of the status of the die material investigations is given below.

Coatings of Silicon Dioxide on Refractory Metals and Silicon Carbide

These coatings were obtained by pyrolysis of silane in the presence of oxygen. The quartz films were too thin and/or too porous to resist molten silicon. This, coupled with a slow deposition rate, led to the abandonment of this technique.

Hot Pressed Silicon Dioxide/Silicon

Orifices were fabricated from hot pressed mixtures of SiO_2/Si in ratios of 5, 10, and 30% Si. These orifices were all unsuccessful because of the low strength of the mixtures. Tests of the wettability of these materials by silicon showed a tendency for the silicon within the structure to run out when molten and for the material to warp when it was in pieces the thickness of typical orifices. This technique has been abandoned.

Silicon Dioxide/Silicon Carbide

A slice of hot-pressed 80% quartz/20% silicon carbide with a small silicon chip was heated to approximately 1650°C, which is the typical temperature used to prewet orifices, for 10 min then cooled approximately to 1,450°C, typical of operating growth temperatures. The samples were held for 50 min at the 1,450°C temperature before cooling to room temperature. The silicon was found to wet the surface of the slice completely, stopping at only a few mils of penetration of the silicon into the bulk of the slice. In addition, the surface of the solid silicon left was very clean, without the ordinary haze of tiny reprecipitated silicon carbide crystals found when a similar experiment was done on silicon carbide material. Orifices of this material are currently being fabricated and evaluated.

Beryllium Oxide

The use of beryllium oxide will represent the first effort in evaluating entirely new die materials. It has been reported that beryllium dopes silicon P-type, so that if beryllium does tend to leach out into the silicon, it will at least be doping it in the proper direction. Experiments in this material have not yet been initiated but will be begun in the near future.

Silicon Carbide

The first attempts to grow silicon ribbon on this program were made utilizing pressed and sintered silicon carbide as the die material with quartz as the crucible material. Silicon carbide was wet by the silicon, and little difficulty was encountered in obtaining the initial capillary rise required for a growth initiation. This was found to be especially facilitated when the silicon carbide was "pretinned" with liquid silicon before assembling into the shaping-die configuration. The resistivity of these initial ribbons was low, of the order of 0.1 Ω-cm, possibly due to either the leaching of impurities from the silicon carbide or from dissolution of the silicon carbide itself, the latter being observed upon inspection of the shaping-die after growth.

Initial dies fabricated from silicon carbide appeared to undergo severe degradation during the growth process and formed inclusions in the grown silicon ribbon. Also the resistivity of the resultant silicon was very low indicating contamination of the silicon by the die material. More recently, samples of various silicon carbide materials made by the conversion of graphite were evaluated by melting silicon on a piece of the material and holding it at a temperature typical of growth conditions. One material was clearly superior to the others in that it appeared to be very dense, and the wetting of molten silicon was confined to the surface.

Graphite

The most recent very positive results, of the nature of a breakthrough, have been obtained by utilizing a die fabricated from high-density, small-grain-size graphite material. Using this die in conjunction with a thicker molybdenum cover plate for increased thermal stability, ribbons having dimensions of 1 cm wide by 30 cm long with a thickness of about 0.7 mm have been grown. Cursory examination of the die indicated essentially no deterioration. This was further evidenced by measurement of 2- to 3-Ω-cm resistivity at several points along the ribbon, indicating that at least there was no gross contamination of the silicon by the die. More extensive evaluation of the crystalline properties of these ribbons will be undertaken in the near future; however, the success of the silicon ribbon program to date is encouraging.

Conclusions

A breakthrough in the growth of thick-film silicon ribbons by means of the EFG process has been achieved through improvement of thermal and mechanical growth system stability and through development of a shaping die fabricated from high-density, small-grain-size graphite material. Ribbons having dimensions of 1 cm wide by 30 cm long, and a thickness of approximately 0.7 mm have recently been grown as a result of these improvements. The suitability of these ribbons for solar cell materials still has to be evaluated.

This development program, if successful, could have an impact solar array fabrication technology, resulting in improved array fabrication techniques. The solar cells fabricated from large-area films, grown by means of the technique discussed, potentially can result in significant improvements in power density, weight, and economics. Furthermore, rather than fabricating an array from a large number of relatively small (4 cm^2 is the most commonly used size) solar cells and interconnecting them together, the array could possibly be made of a far fewer number of cells, each having lengths of 20 cm, 30 cm, or even more.

If successfully developed, the described ribbon cell could be used to produce large-area, highly efficient, lightweight, economical solar arrays, and therefore would be particularly advantageous where these characteristics are of prime importance. The improved economics that could be realized through solar cell and array fabrication processes geared to take advantage of the large-area silicon ribbons would also enhance the feasibility of wide-scale, Earth-based solar photovoltaic electrical power generating systems (e.g., solar farms and rooftop solar-electric generators).

References

1. Berman, P. A., *Considerations with Respect to the Design of Solar Photovoltaic Power Systems for Terrestrial Applications,* Technical Report 32-1556. Jet Propulsion Laboratory, Pasadena, Calif., June 15, 1972.

2. Berman, P. A., *Photovoltaic Solar Array Technology Required for Three Wide-Scale Generating Systems for Terrestrial Applications: Rooftop, Solar Farm, and Satellite,* Technical Report 32-1573. Jet Propulsion Laboratory, Pasadena, Calif., October 1972.

3. Ralph, E. L., "Large Scale Solar Electrical Power Generation," presented at the Solar Energy Society Conference, NASA Goddard Space Flight Center, Greenbelt Md., May 1971.

4. Berman, P. A., *High Efficiency Silicon Solar Cells,* Report No. VIII, Final Report. Contract No. DA 36-039-SC-907, covering period from June 1962 to July 1964. U.S. Army Electronics Laboratories, Fort Monmouth, N.J.

5. Berman, P. A., "Design of Solar Cells for Terrestrial Use," presented at the Solar Energy Conference, Boston, Mass., March 1966. Published in *Solar Energy,* Vol. 11, Nos. 3 and 4, 1967.

6. Glaser, P. E., "Power from the Sun," *Mech. Eng.,* Vol. 91, No. 3, March 1969.

7. Ralph, E. L., and Benning, F., "The Role of Solar Cell Technology in the Satellite Solar Power Station," in *Conference Record of the Ninth IEEE Photovoltaic Specialists Conference, Silver Springs, Md., May 1972.*

8. Bates, H. E., Cocks, F. H., Mlavsky, A. I., "The Edge-Defined, Film-Fed Growth (EFG) of Silicon Single Crystal Ribbon for Solar Cell Applications," in *Conference Record of the Ninth IEEE Photovoltaic Specialists Conference, Silver Springs, Maryland, May 1972.*

9. Bates, H. E., Cocks, F. H., Mlavsky, A. I., *Thick Film Silicon Growth Techniques: First Quarterly Progress Report,* JPL Contract 953365,

covering period February-May 1972. Tyco Laboratories, Waltham, Mass.

10. Bates, H. E., et al., *Thick Film Silicon Growth Techniques: Second Quarterly Progress Report,* JPL Contract 953365, covering period June-August 1972. Tyco Laboratories, Waltham, Mass.