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THIN FILM POLYCRYSTALLINE SILICON SOLAR CELLS

MASTER

First Technical Progress Report for April 15, 1980—July 15, 1980

July 1980

Work Performed Under Contract No. AC02-77CH00178

Poly Solar Incorporated
Garland, Texas

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First Technical Progress Report

Covering the Period April 15, 1980 to July 15, 1980

Prepared under SERI Subcontract XZ-ϕ-9192-1

by

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July, 1980

CONTENTS

List of Illustrations

List of Tables

Summary

This is the First Technical Progress Report of a research program "Thin Films Polycrystalline Silicon Solar Cells" supported by the Solar Energy Research Institute under Subcontract No. XZ-ϕ-9192-1. The objectives of this contract are to fabricate large area thin film silicon solar cells with AM1 efficiency of 10% or greater with good reproducibility and good yield and to assess the feasibility of implementing this process for manufacturing solar cells at a cost of $300/kWe.

Efforts during the past quarter have been directed to the purification of metallurgical silicon, the preparation of substrates, and the fabrication and characterization of solar cells. The partial purification of metallurgical silicon by extraction with aqua regia has been investigated in detail, and the resulting silicon was analyzed by the atomic absorption technique. The unidirectional solidification of aqua regia-extracted metallurgical silicon on graphite was used for the preparation of substrates, and the impurity distribution in the substrate was also determined.

Large area (>30 cm^2) solar cells have been prepared from aqua regia-extracted metallurgical silicon substrates by the thermal reduction of trichlorosilane containing appropriate dopants. Chemically deposited tin-dioxide films were used as antireflection coatings. Solar cells with AM1 efficiencies of about 8.5% have been obtained. Their spectral response, minority carrier diffusion length, and I_{sc}-V_{oc} relation have been measured.

I. Introduction

This is the First Technical Progress Report of a research program "Thin Films Polycrystalline Silicon Solar Cells" supported by the Solar Energy Research Institute under Subcontract No. XZ-ϕ-9192-1. The objectives of this contract are to fabricate large area thin film silicon solar cells with AM1 efficiency of 10% or greater with good reproducibility and good yield and to assess the feasibility of implementing this process for manufacturing solar cell at a cost of $300/kWe.

The principal approach used in this work is the deposition of a silicon film of controlled thickness and dopant concentration on a partially purified metallurgical silicon substrate by the thermal reduction of trichlorosilane, the most economical process for the manufacture of polycrystalline silicon. Metallurgical silicon was selected as the substrate because of its crystal structure and low cost. During the first quarter of this program, efforts were directed to (1) the purification of metallurgical silicon, (2) the preparation and characterization of metallurgical silicon substrates, (3) the deposition and characterization of silicon films on metallurgical silicon substrates, and (4) the fabrication and characterization of silicon solar cells on purified metallurgical silicon substrates. The experimental procedures and results are summarized in the following sections.

II. Purification of Metallurgical Silicon by Acid-Extraction

The principal approach to the fabrication of solar cells used in this program is the deposition of the active region of the cell, a p-n junction, on a purified metallurgical silicon substrate. The development of low cost techniques for the purification of metallurgical silicon and the preparation of large grain substrates from partially purified material is essential for the eventual success of this approach. Commercially available metallurgical silicon is of about 98% purity. Iron and aluminum at concentrations of a few tenths of one percent are the major impurities, and other metallic impurities include boron, chromium, copper, manganese, nickel, titanium, vanadium, zirconium at concentration of up to several hundred parts per million. The impurity content in metallurgical silicon is excessive for device purposes. The current process used in semiconductor industry for the purification of metallurgical silicon consists of (1) the conversion of metallurgical silicon into trichlorosilane by reaction with hydrogen chloride, (2) the purification of trichlorosilane, and (3) the reduction of trichlorosilane with hydrogen. This sequence of processing is tedious, and step (3) is extremely energy-intensive increasing the cost of silicon by about seventy times. Because of this high cost of purification via the halide intermediate, several direct purification techniques have been attempted during the fifties. They include:

(A) The treatment of molten silicon with gaseous chemical reagents to selectively remove specific impurities from the melt.(1) It has been claimed that molten silicon could be purified by treatment with a mixture of halogen (or a halogen derivative) and oxygen, and that 3 kg of technical grade silicon (98%) was purified to 99.99% purity in only 3 min. by the reaction with an equi-molecular mixture of oxygen and hydrogen chloride.(1) However, this result is in contradiction with thermochemical considerations and cannot be reproduced.(2) Chemical treatment is effective for the preferential removal of elements more reactive than silicon, such as aluminum and titanium, and cannot reduce the concentration of iron or copper in silicon due to the stronger reactivity of silicon. The low iron content reported by others (1) could have caused by improper sampling techniques since the solidified material after chemical treatment is highly inhomogeneous due to the small segregation coefficients of metals in silicon. Furthermore, the chemical treatment of the melt is energy-intensive and may not be sufficiently economical for large scale operations.

(B) The remelting of silicon under a layer of fused silicate which getters various impurities.(3) For example, chemical analysis has shown that after three hours of treatment, the concentrations of iron and aluminum were reduced from 4.5% and 1.80% to 1.20% and 0.83%, respectively. This process is also energy-intensive, and the cost of the crucible is also an important consideration.

(C) The treatment of pulverized metallurgical-grade silicon with aqua regia, sulfuric acid, hydrogluoric acid, etc., producing silicon suitable for microwave diodes. (4)

On the basis of the above considerations, acid-extraction appears to be the most economical technique for the purification of metallurgical silicon. Metallurgical silicon is manufactured by the reduction of sand with carbonaceous reducing agents in a submerged electric are furnace at 1700°-1900°C, and the resulting silicon melt is discharged into molds for solidification. While most metallic impurities such as iron, aluminum, copper, etc., are highly soluble in molten silicon, their solubilities in solid silicon are very low.(5) Thus, during the solidification of molten metallurgical silicon in the manufacturing process, a major portion of the metallic impurities should precipitate at grain boundaries or at interstitial positions. The treatment of pulverized metallurgical silicon with acids could dissolve the impurities at grain boundaries. The effectiveness of this technique depends on the particle size of metallurgical silicon, the chemical reactivity of the acid, and the temperature and during of treatment.

A series of aqua-regia extraction experiments have been carried out using the standard procedure developed at Poly Solar. Metallurgical silicon of 30-80 mesh in size was used. About 1.5 kg of metallurgical silicon and 2.5ℓ of aqua regia were refluxed for 100 hours. The aqua regia was replaced and the refluxing continued for another 100 hours. This process was repeated two more times, and the total time of aqua regia treatment was 400 hours. Subsequently, the metallurgical silicon was rinsed with deionized water, digested in a diluted hydrofluoric acid solution to remove the surface oxide, rinsed again with deionized water, and dried. The impurity contents in as-received metallurgical silicon and metallurgical silicon after 400 hours of aqua regia treatment were determined by emission spectrographic and atomic absorption techniques. The average concentrations of a number of impurities determined by at least three analysis are shown in Table I. The emission spectrographic analysis and atomic absorption analysis are in poor agreement in most cases; however, the concentrations of iron and aluminum, the most common impurities in metallurgical silicon, obtained by the two techniques are similar.

The concentration of impurities in each aqua regia extract, determined by the atomic absorption analysis, is summarized in Table II. In addition to the standard purification technique, a series of experiments were also carried out in which the duration of refluxing was reduced from 100 hours to 24 hours after each acid change in order to determine the effects of the

Table I. Concentration of impurities (ppma) in as-received metallurgical silicon and metallurgical silicon purified by aqua regia-extraction determined by emission spectrographic and atomic absorption analysis.

	Metallurgical Silicon		MG Silicon after aqua regia treatment	
Element	Emission Spect.*	Atomic Absorp.**	Emission Spect.	Atomic Absorp.
Al	>500	610	250	320
B	10	-	10	-
Ba	< 50	-	< 50	-
Ca	<100	-	< 100	-
Cd	<0.5	-	< 0.5	-
Co	< 50	-	< 50	-
Cr	< 50	-	< 50	-
Cu	75	10	50	5
Fe	>500	1,500	500	350
Mg	< 50	-	< 50	-
Mn	100	40	50-75	10
Mo	< 50	-	< 50	-
Ni	500	25	300	15
Pb	< 50	-	< 50	-
Sn	< 50	-	< 50	-
Sr	<100	-	< 100	-
Te	<100	-	< 100	-
Ti	150	N.D.	75-100	N.D.
V	500	N.D.	200-300	N.D.
W	500	-	300-500	-
Zn	<100	-	< 100	-
Zr	20	N.D.	< 10	N.D.

*< Means less than the sensitivity of the spectrographic procedure used. Results are correct within a factor of two of the amount present.

** N.D. = not detectable

- not analyzed.

duration of aqua regia treatment. The impurity concentration in these aqua regia extracts is also summarized in Table II. It is apparent that the major portion of extractable impurities is removed by the first acid-treatment and that longer duration of refluxing is more effective. The total amount of iron removed is 0.175% and 0.122% (weight) after 400 hours and 100 hours of extraction, respectively, and the total amount of aluminum removed is 0.69% and 0.5%, respectively. These results are in qualitative agreement with the concentrations of iron and aluminum in the starting material and in the metallurgical silicon after 400 hours of aqua regia-extraction. Also, an appreciable amount of iron and nickel is present in the fourth extract, indicating that further extraction would be useful.

Table II. Concentration of impurities (mg/liter) in the aqua regia-extract after refluxing with metallurgical silicon for various duration

Metal	Hours of aqua regia extraction				Hours of aqua regia extraction			
	100	200	300	400	24	48	72	96
Aluminum	670	14.2	4.1	3.1	470	25.4	2.1	0.80
Iron	1,430	135	76	112	860	136	120	102
Copper	13.8	0.31	0.33	0.24	10.2	0.53	0.31	0.25
Manganese	4,780	10.7	3.9	2.7	169	11.4	8.6	3.0
Nickel	35.6	10.6	11.7	11.2	5.0	12.3	14.5	11.4
Vanadium	3.1	0.3	0.2	0.1	0.9	0.2	0.1	>0.1
Titanium	16.7	1.1	0.7	0.5	7.6	1.1	0.4	0.4

III. Preparation and Characterization of Metallurgical Silicon Substrates

The preparation of metallurgical silicon substrates is a most important processing step in the fabrication of thin film polycrystalline silicon solar cells. When a metallurgical silicon substrate is used for the deposition of the active region of the solar cell, the chemical and structural defects in the substrate greatly affect the characteristics of the solar cell. A unidirectional solidification technique has been used in this program to prepare substrates from the metallurgical grade silicon purified by aqua regia-extraction. This technique is briefly as follows. The purified metallurgical silicon is placed on a graphite plate with a sandblasted surface of 7.5 cm x 28 cm area; the roughened surface is used to increase the graphite-molten silicon interfacial tension. This assembly is then placed in a fused silica tube of 10.5 cm ID and heated externally by an rf generator. The spacings between the turns of the rf coil are adjusted to yield a unidirectional temperature gradient of 80°-100°C along the length of the specimen. The entire specimen is first melted, and the input power reduced for the solidification to take place from one end of the specimen to the other. The solidification initiates from the surface of the melt and proceeds inwards to minimize the orienting effects of polycrystalline graphite.

The rate of solidification is the most important parameter in the unidirectional solidification technique. At relatively high rate of solidification, about 5 cm/min, the resulting surface is not planar but has many ridges, faces, and valleys. The non-planar surface is undesirable for subsequent processing, such as contact formation. Planar surfaces were obtained by using a lower rate of solidification, 1 cm/min for example. By controlling the thermal conditions, a planar solid-liquid interface has been obtained. The resulting substrate consists of elongated crystallites of several centimeters long. Optical and scanning electron microscopic examinations of chemically etched surface indicate that grain boundaries, multiple twins, and dislocations are major defects in the metallurgical silicon substrates.

The crystallographic properties of several metallurgical silicon substrates have been investigated by the x-ray diffraction technique using CuK_α radiation. Polycrystalline silicon of random orientations is known to show three strong diffraction peaks associated with {111}, {220}, and {311} reflections with 2θ values of 28.4°, 37.3°, and 56.1°, respectively. Many areas have been found to show a very strong {110} preferred orientation, and no {111} and {311} reflections were detected. In other areas, however, a very strong {331} preferred orientation was observed. Examples of these preferred orientations are shown in Fig. 1.

The impurity concentration and distribution in a metallurgical silicon substrate have been investigated in detail by Dr. Lawrence L. Kazmerski of the Solar Energy Research Institute using Auger and SIMS techniques. A strip of about 2 cm width was cut from the center region of the substrate along its length, and this strip was further cut into twelve pieces of about 2 cm length. Each piece was examined by the AES and SIMS techniques. Preliminary analysis of the AES and SIMS data indicates that the impurity distribution in the substrate is reasonably uniform and that the concentrations of most impurities in the substrate is at least an order of magnitude lower than those in metallurgical silicon. Detailed results will be discussed in the next quarterly report.

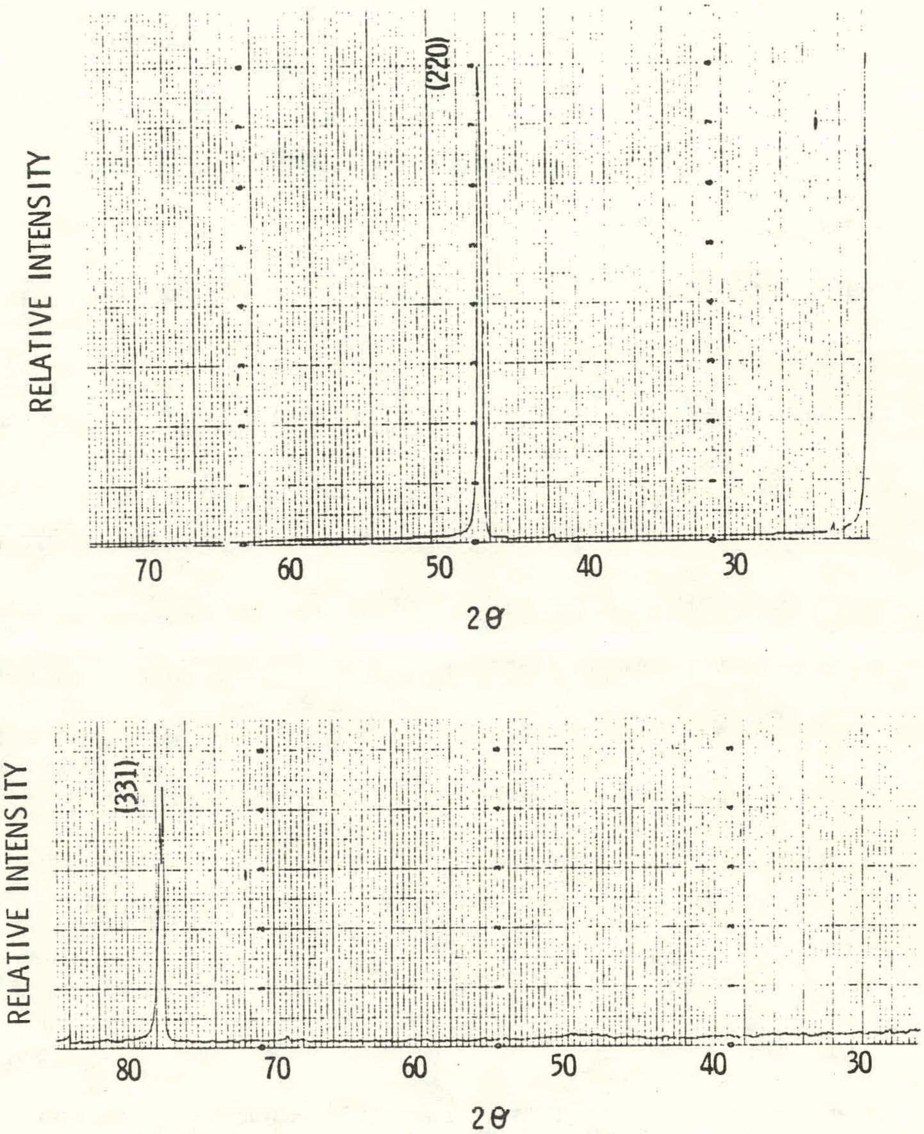

Figure 1 X-ray diffraction spectra of a metallurgical silicon substrate showing {110} (upper) and {311} (lower) preferred orientations.

IV. Silicon Films on Metallurgical Silicon Substrates

The active region of the solar cell is formed by the chemical vapor deposition of a silicon film containing a p-n junction with controlled dopant concentration and distribution on a metallurgical silicon substrate. The CVD technique is superior to the conventional diffusion technique in several aspects. The dopant concentration and distribution in vapor deposited silicon can be programmed and controlled to an extent not obtainable by the diffusion technique. The vapor deposited silicon films also has better chemical and structural perfection than the diffused material; defects, such as precipitates, dislocation clusters, stress, etc., are often introduced into the p-n junctions by diffusion process.

IV.1 Control of Properties of Silicon Films

The structural perfection, the thickness and thickness uniformity, and the dopant concentration and distribution are the most important properties of the silicon films affecting the operation of devices. The structural perfection of the silicon film grown under proper conditions of substrate temperature and growth rate is determined predominately by the cleanliness of the substrate surface, the purity of the reactants, and the structural perfection of the substrate. Essentially all structural defects in the substrate, except the dislocations parallel to the substrate surface, will propogate into the film. Further, contaminants in the reactant mixture, mechanical damage in the substrate, and foreign impurities on the substrate surface will generate structural defects at the substrate-film interface, and these defect will propogate into the deposited films. In-situ etching techniques using hydrogen chloride are generally used to provide clean substrate surfaces for the growth process. Silicon films with structural perfection similar to that of the substrate can readily be obtained.

The deposition rate of silicon films depends on the reactant composition and its flow rate, the substrate temperature, and the gas flow characteristics over the substrate surface. Under a given set of conditions, the thickness of the silicon film is a linear function of time and can thus be controlled. The thickness uniformity of silicon films can be controlled by maintaining a uniform gas flux over substrate surfaces. This is usually accomplished by using a high gas flow rate and proper geometrical arrangement of substrates in the reaction tube.

The electrical resistivity of the silicon films is determined predominately by the impurity content of the reactant and the purity of the growth apparatus. When the thermal reduction of a silicon halide, such as silicon titrachloride or trichlorosilane, is used for the deposition of silicon films, the resistivity of the substrate may also be significant. For example, the substrates are usually supported on a coated graphite susceptor which also functions as a heater. Since the halide process is chemically reversible and many other elements also react reversibly with hydrogen chloride at high temperatures, silicon and impurities can be transported from the susceptor or the backside of the substrate to the growing surface. The transport may take place to a marked degree during the initial deposition and to a lesser degree during the later stage of deposition. When the effects of the growth apparatus and substrates are minimized, controlled addition of dopants into the reactant can yield silicon films of desired resistivities. Hydrides of the group III and V elements are versatile dopants to provide both n-and p-type films in the resistivity range of 0.001 to 100 ohm-cm, and the resistivity of highly doped films can be controlled better than that of high resistivity films. Furthermore, graded junctions and multijunction structures can be produced by programmed introduction of dopants. The resistivity uniformity of the silicon films can be controlled by providing the same dopant concentration over all substrate surfaces. Techniques used for achieving the thickness uniformity could also minimize the resistivity variations.

IV.2 Experimental and Results

The thermal reduction of trichlorosilane, the most economical process for the manufacture of polycrystalline silicon, has been used for the deposition of silicon films on metallurgical silicon substrates in this program. Emphasis is directed to the improvement of structural properties, thickness uniformity, and dopant concentration and profile in the silicon film.

The apparatus for the deposition of silicon films consists of a fused silica tube of 10.5 cm ID. The metallurgical silicon substrate was placed on a fused silica holder in this tube and was tilted at an angle of 3-4° to minimize thickness variations in the silicon films. The substrate was heated externally by an rf generator. Prior to the deposition process, the substrate was first heated in hydrogen at about 1200°C to remove the oxide films on the surface; the oxide film reacts with silicon underneath to form volatile silicon monoxide. In many cases, the substrates were further etched with anhydrous hydrogen chloride to remove 2-3 μm of silicon from the substrate surface. The deposition of silicon was then carried out at a substrate temperature of 1100°C using hydrogen containing trichlorosilane at a flow rate of 40 ℓ/min. The concentration of trichlorosilane in the reactant mixture was adjusted to yield a deposition rate of about 1 μm/min. A series of experiments were carried out to determine the relation between the flow rate of dopant, phosphine and diborane, and the resistivity of the silicon film. The resistivity range of interest for solar cell purposes is 0.003-1 ohm-cm.

The structural perfection of silicon films was evaluated by chemical etching and optical microscopy. In general, the microstructure of the silicon film is essentially the same as that of the substrate. A number of experiments were carried out to determine the effects of process parameters on the thickness and resistivity uniformity of the film. Under the conditions described above, the thickness of silicon film is uniform within 10%, and its resistivity is uniform within 15%. For example, the thickness measured along the length of a phosphorus doped film (deposited time: 20 min) is 19 ± 0.5 μm, and the thickness across the width of the specimen is 19 ± 1 μm. The electrical resistivity measured along the length of the specimen is 0.0024 ± 0.002 ohm-cm.

V. Thin Film Polycrystalline Silicon Solar Cells

During this reporting period, more than 100 large-area solar cells (35 cm^2 or larger) have been prepared by the deposition of the active region on metallurgical silicon substrates. Solar cells of the configuration n^+ -silicon/p-silicon/p^+ -metallurgical silicon (acid-extracted)/graphite were prepared by the trichlorosilane process using diborane and phosphine as dopants. The low resistivity substrate serves to minimize the contact resistance between silicon and graphite and also provides a back-surface field. The p-n juntion was formed during the deposition process by varying the composition of the reactant mixture. Typically, 20-30 μm of 0.2-1 ohm-cm p-type silicon was deposited at 1100°-1150°C at a rate of about 1 μm/min followed by the deposition of about 1-10 μm of n-type silicon at the same rate. The resistivity of the n-layer was varied according to its thickness, and its sheet resistance is 40-50 ohms per square. The effects of the thickness of the n-layer on the characteristics of solar cells have not been evaluated. The graphite plate serves as the ohmic contact to the p-region. The grid contact to the n^+-surface, 4 lines per cm, was made by evaporating about 1000 Å of titanium and 2-3 μm of silver to the cell surface through a metal mask, followed by annealing in a hydrogen atmosphere at 500°C. Subsequently, antireflection coatings were applied by the deposition of approximately 750 Å of tin oxide.

Solar cells prepared in this work were usually of 35 cm^2 in area. Their characteristics were measured at room temperature according to the standard procedures. The characteristics of solar cells are affected strongly by the structural perfection of the substrates. During the early stage of this program, the substrate had high concentrations of structural defects, such as silicon carbide inclusions, and the AM1 efficiency of solar cells was only 3-4%. As the quality of the substrate improved, the efficiency of the solar cells increased. The best cell to date has an AM1 efficiency of about 8.5%. Figure 2 shows the illuminated current-voltage characteristics of a solar cell of about 35 cm^2 area. The illumination was provided by four GE ELH quartz halogen lamps calibrated to AM1 conditions. The open-circuit voltage, short-circuit current density, and fill factor are 0.58 V, 20 mA/cm^2, and 0.74, respectively, corresponding to a conversion efficiency of about 8.5%. The series resistance of the cell, deduced from the current-voltage characteristics under different illumination levels, is about 0.04 ohms.

The spectral response of a number of thin film solar cells has been measured using eleven interference filters with peak transmission at 0.4, 0.45, 0.5, 0.6, 0.7, 0.8, 0.85, 0.9, 0.95, 1.0, and 1.014 μm. It is measured in terms of the short-circuit current, in milliamperes, divided by the incident optical power, in milliwatts, at a specific wavelength. Figure 3 shows the spectral response of the solar cell shown in Figure 2 together with that of a calibrated cell for comparison. The peak response for the thin films cell occurs at a shorter wavelength than that for the single crystalline cell. In addition, the quantum efficiency in the thin film cell is lower than that in the single crystalline cell. The shift in peak response and lower quantum efficiency is not unexpected in view of the small thickness of the active region of, and the relative short minority carrier diffusion in, the thin film cell. The effective minority carrier diffusion length in thin film cells is in the range of 20-25 μm.

Figure 4 shows the short-circuit current and open-circuit voltage relation of the thin film cell shown in Fig. 2. The diode quality factor is about 2 at voltages between 0.4 and 0.5V, and decreases at higher voltages. As a comparison, the short-circuit current and open-circuit voltage relation of a single crystalline silicon solar cell is shown in Figure 5.

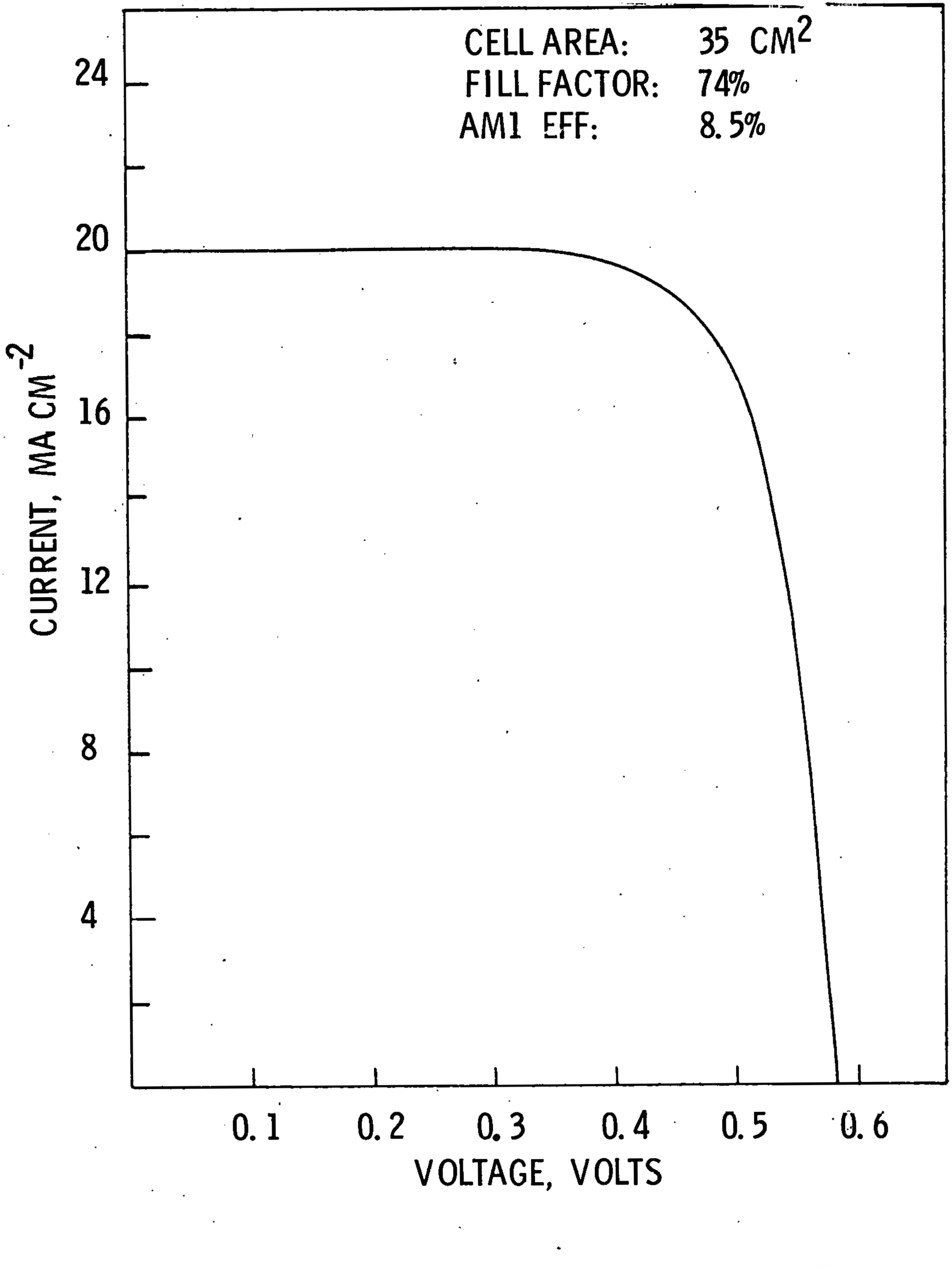

Figure 2 Current-voltage characteristics of a large area polycrystalline thin film silicon solar cell under illumination with GE ELH quartz-halogen lamps equivalent to AM1 conditions.

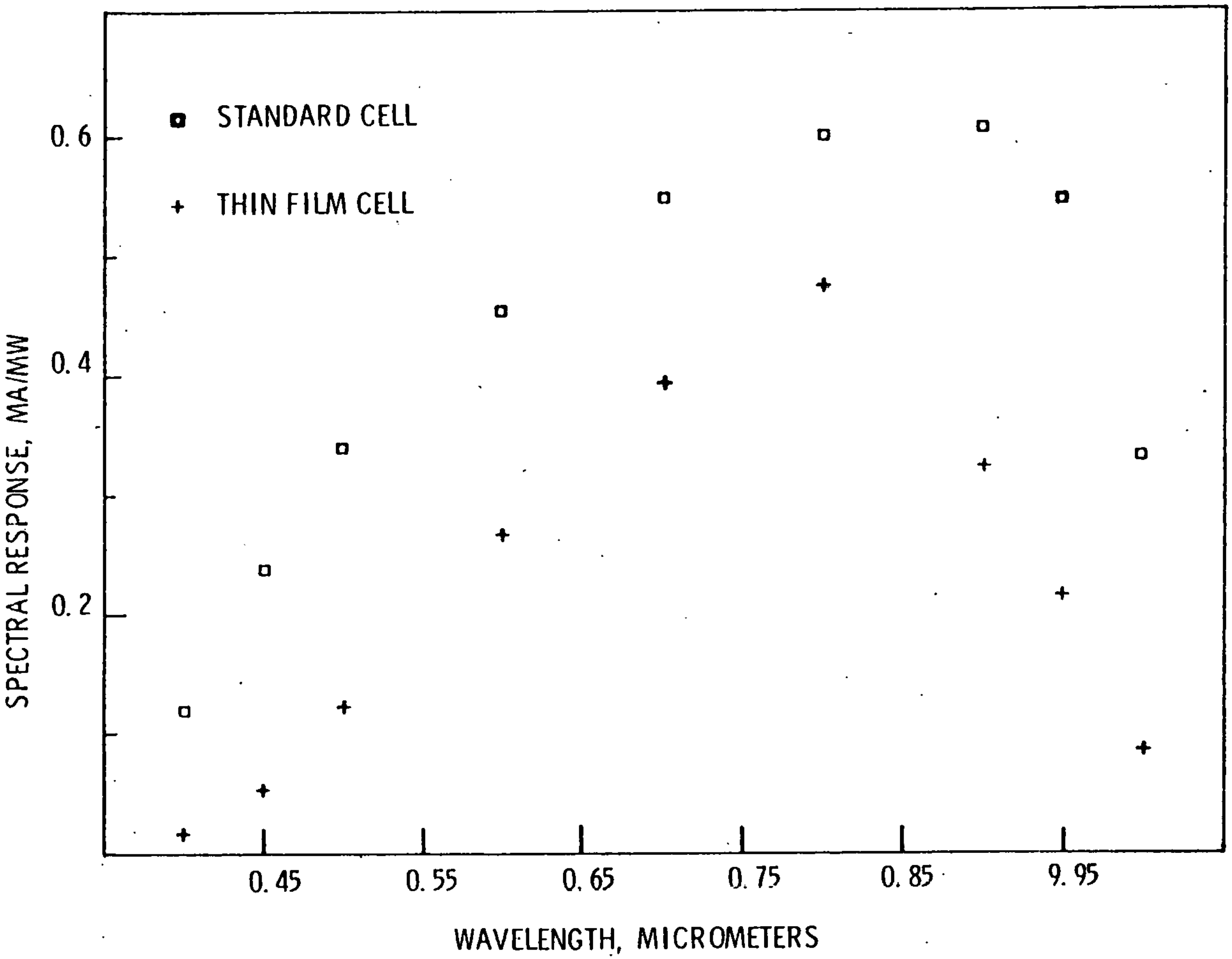

Figure 3 Spectral response of the thin film silicon solar cell shown in Figure 2.

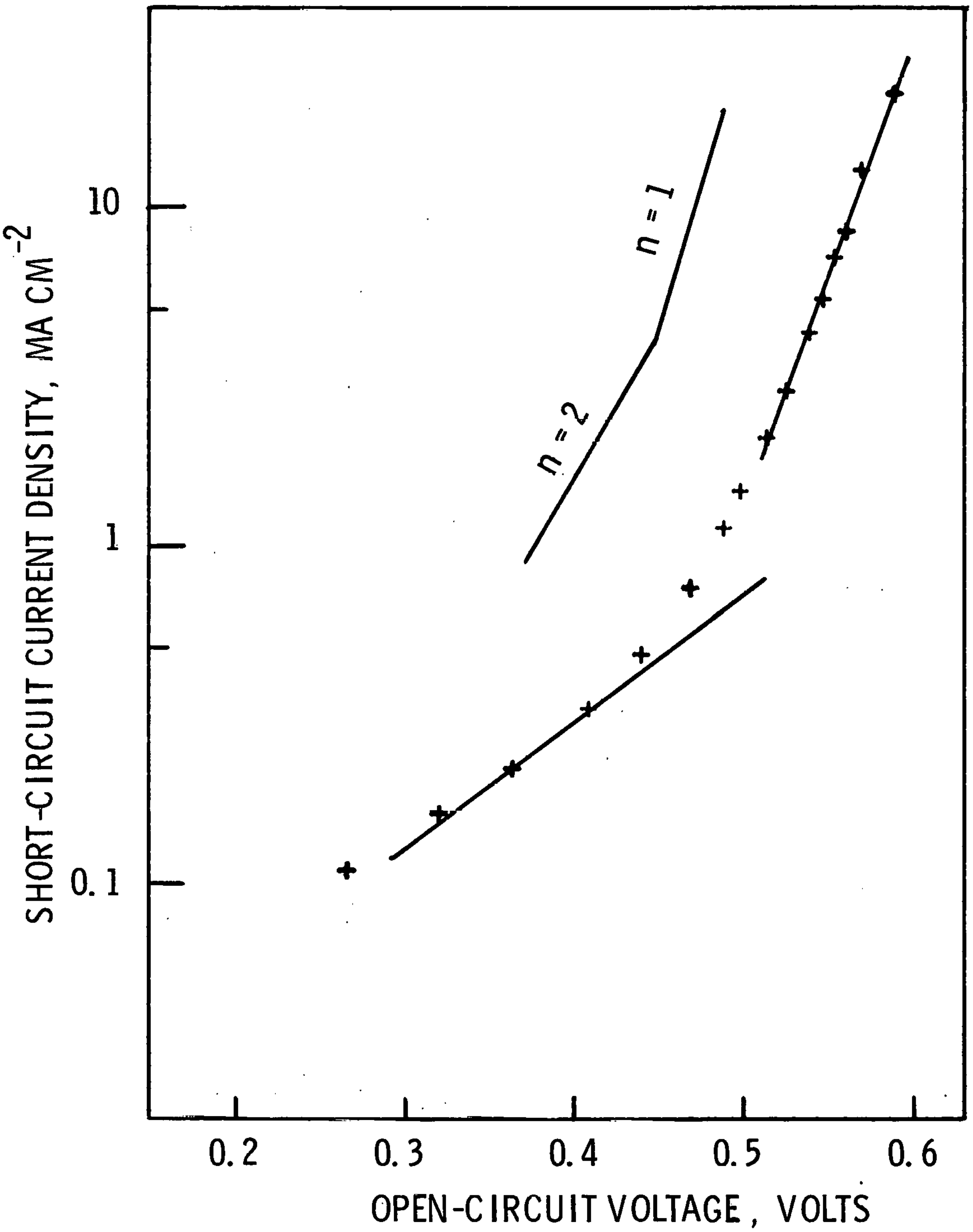

Figure 4 Short-circuit current and open-circuit voltage relations of the thin film silicon solar cell shown in Figure 2.

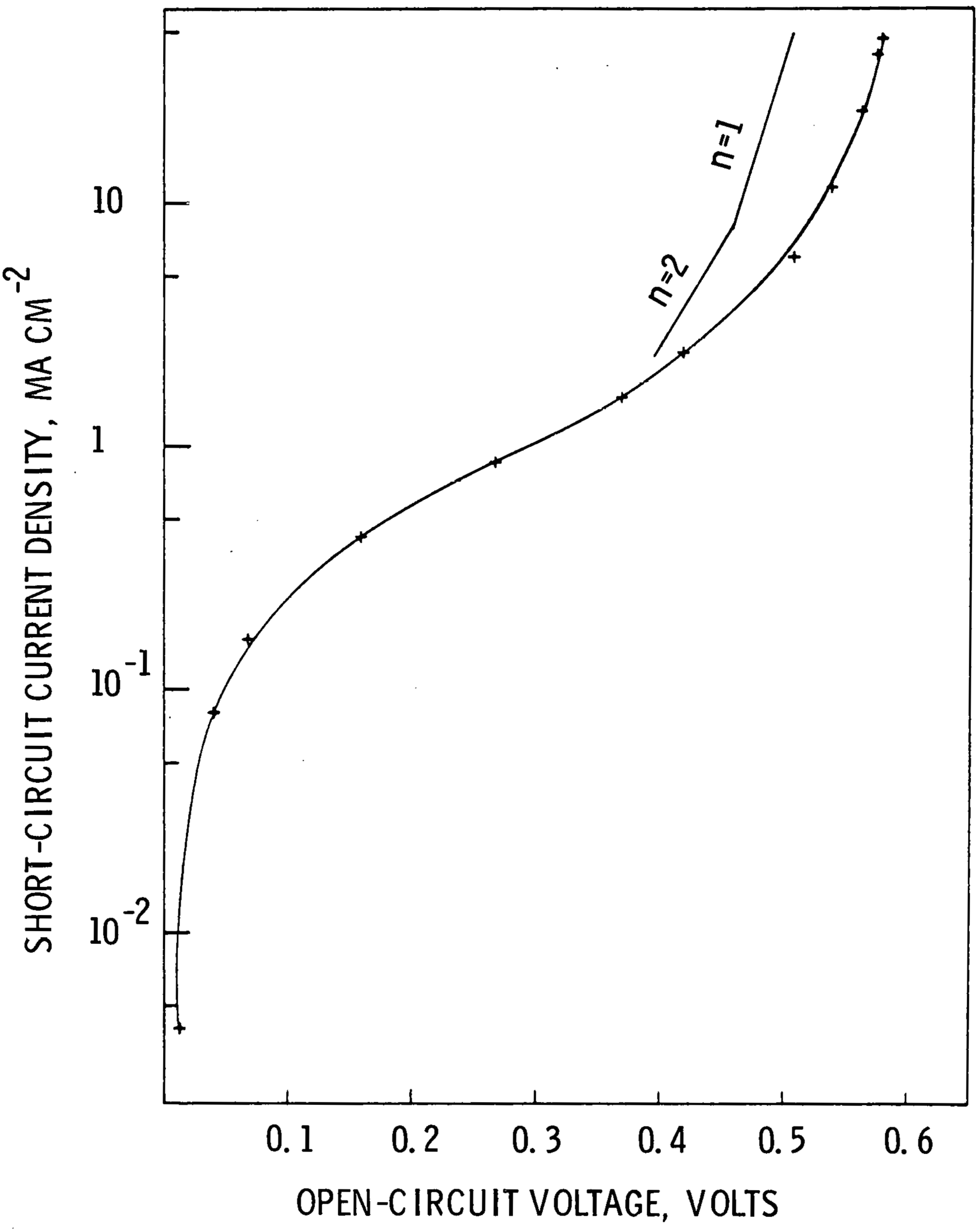

Figure 5 Short-circuit and open-circuit voltage relations of a single crystalline silicon solar cell of 4 cm^2 area with an AM1 efficiency of about 15%.

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VII. Plan For The Next Period

1. Further optimization of the purification of metallurgical silicon.
2. Improvement of the preparation of metallurgical silicon substrate.
3. Deposition and characterization of silicon films on metallurgical silicon substrates.
4. Fabrication and characterization of solar cells.

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