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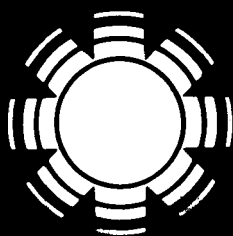
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# Deposition of Amorphous Silicon Solar Cells at High Rates by Glow Discharge of Disilane

## Final Subcontract Report January 1985 - July 1986

**P. E. Vanler**  
Brookhaven National Laboratory

Prepared under Project No. DS-0-9055-1,  
Contract No. DE-AC02-76CH0016  
to the U.S. Department of Energy  
for the Solar Energy Research Institute



# SERI

**Solar Energy Research Institute**

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# **Deposition of Amorphous Silicon Solar Cells at High Rates by Glow Discharge of Disilane**

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**January 1985 - July 1986**

**P. E. Vanier**  
Brookhaven National Laboratory

SERI Technical Monitor:  
**Werner Luft**

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## PREFACE

This report summarizes the results of amorphous silicon (a-Si:H) thin film photovoltaic (PV) materials research carried out during the last 18 months for the United States Department of Energy (DOE) at Brookhaven National Laboratory (BNL), monitored and coordinated with the national PV effort by the Solar Energy Research Institute (SERI). Funding for the work was transferred within DOE from SERI to BNL.

This program, which started in FY 1980 under the title "Advanced Amorphous Materials For Photovoltaic Conversion" has included studies of several areas relevant to amorphous silicon technology, including (1) the study of glow discharge plasmas by optical emission spectroscopy, (2) characterization of a-Si:H films by temperature dependent photoconductivity measurements (displaying a number of new interesting features), (3) observation of important effects of impurities on a-Si:H properties, and (4) deposition of both n-type and p-type microcrystalline silicon layers.

The most recent work concerns the fabrication of a-Si:H solar cells at high deposition rates using disilane. This task required the construction of new dual-chamber deposition system to control the dopant profile between the heavily doped p-type layer and the undoped (intrinsic) layer in the solar cell structure. Conditions were sought which would produce high quality films at high deposition rate, and complete photovoltaic devices were fabricated.

Most of the dual chamber deposition system was designed and constructed by Dr. Frank Kampas. The first set of experiments, using disilane diluted in helium, was carried out by Dr. G. Rajeswaran. Subsequent depositions were performed by Frank Thomsen and Feng-Cheng Su, who also carried out many of the measurements. The principal investigator of the project is Dr. Peter Vanier.

## SUMMARY

### OBJECTIVES

The use of disilane ( $\text{Si}_2\text{H}_6$ ) in the glow-discharge deposition of the intrinsic layers of a-Si:H solar cells offers the advantage of high deposition rates, and therefore a large throughput for a production facility. However, fabricating efficient devices at high rates (1.5-2.0 nm/s) using disilane is considerably more difficult than making them at low rates (0.10-0.30 nm/s) using silane ( $\text{SiH}_4$ ). The purpose of this research was to determine appropriate deposition procedures for making reasonably good solar cells at high rates using disilane glow discharges, and to find out the basic factors which limit the efficiency of cells made in this way. Since disilane is produced industrially in much smaller quantities than silane, it is much more expensive. Laboratory scale experiments can show whether the disilane process offers advantages over the more traditional silane method, sufficient to justify an increased volume of disilane production.

### DISCUSSION

At the outset, it was recognized that residual dopant species remain in a glow discharge chamber for a considerable time after the deposition of a doped layer. Thus depositing the intrinsic layer of an a-Si:H p-i-n structure at a high rate would exacerbate the problem of incorporation of residual dopant species into the i-layer. A dual-chamber glow discharge system was designed and built from standard ultra-high vacuum components to improve the control of junction formation. One chamber was used for preparing either p-type or n-type layers, and the other was kept as free of dopants as possible. The mechanism for transferring substrates between chambers was also designed and built at BNL. This system has been successful in controlling residual impurities, and is capable of fabricating high quality devices. After more than 500 depositions, it is clear that the system is much more reliable, leak-tight, and flexible in its mode of operation compared to the commercially built (Plasma-Therm) system used in the previous five years of the BNL Amorphous Materials project.

Other problems have been more difficult to solve. Disilane is more prone to gas phase polymerization than silane, tending to generate orange powder at the driven electrode (cathode) of the radio frequency glow discharge chamber. Conditions which avoid this powder formation tend to yield non-uniform films or low deposition rates. At first it appeared that rapid deposition of uniform films could only be achieved under conditions where a considerable amount of powder was formed on the cathode while the film was growing on the grounded electrode (anode). More recently, a narrow range of parameters was found where these problems were avoided. Many cells were fabricated in order to optimize substrate temperature and p-layer composition. Several other parameters, such as layer thicknesses and dopant profiles in the i-layer can still be adjusted to improve efficiency.

## CONCLUSIONS

Using a dual-chamber system, cells have been fabricated at high rates from disilane without powder formation, and compared with cells made from silane in the same system. The substrate temperature is critical in obtaining a low defect density in the intrinsic layer, which is necessary for good fill factors. In disilane deposited material, the optimum substrate temperature is significantly higher than in silane material, presumably because it is more difficult to eliminate the excess hydrogen in the former case. The efficiency of the best disilane cell was about 7 %, with an open circuit voltage of 0.80 V, a short circuit current density of  $14.7 \text{ mA cm}^{-2}$  and a fill factor of 0.59. The most likely area of future improvement is in the voltage, where values as high as 0.9 V should be possible with careful adjustment of the cell structure.

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## SECTION 1.0

### INTRODUCTION

#### 1.1 ECONOMIC JUSTIFICATION

One of the factors limiting the economic success of amorphous silicon (a-Si:H) photovoltaic modules could be the rate of deposition of the intrinsic layer. Typically, high quality intrinsic material is deposited by glow discharge of silane at a rate of about  $0.1 \text{ nm s}^{-1}$ , which means that a layer 500 nm thick takes more than an hour to be deposited. In small batch systems, this may not be the rate-limiting step, since the initial outgassing of the system usually takes more than an hour, and the subsequent fabrication steps such as scribing, metallization, and encapsulation may also be slow. However, in continuously running production lines, the number of megawatts of generating power obtainable in a year of manufacturing will probably be dependent on the i-layer deposition rate. It is therefore important to know how the quality of these thin film devices is affected by increasing the deposition rate.

#### 1.2 HISTORICAL PERSPECTIVE

An increase in deposition rate to  $0.3 \text{ nm s}^{-1}$  has been achieved by diluting silane in hydrogen, at a pressure of  $1 \text{ Torr}$ , without a loss in film quality [1]. Rates as high as  $8.0 \text{ nm s}^{-1}$  have been reported using silane in discharges driven at high power at low frequencies [2] or confined by metal screens [3], but no devices were mentioned. Scott and Brodsky showed that low pressure discharges of disilane produced films at much higher rates than silane discharges [4], but their results were obtained in an inductively coupled system, which is not as easily scalable to large areas as the now-common capacitively coupled systems. The diffusion distances of different film precursors in silane and disilane discharges were measured by Matsuda and co-workers [5]. Early attempts to fabricate solar cells using disilane showed that it was difficult to achieve the same efficiency as with silane [6]. Later, solar cells with high efficiencies deposited at high rates from disilane-helium mixtures were reported [7,8], but the conditions used tend to cause considerable gas phase polymerization [9].

#### 1.3 DIFFICULTIES

The formation of thick deposits of polysilane powder in the discharge chamber discourages further development of an industrial process based on disilane. However, if the substrates are suspended from the upper electrode it is possible to grow good films at high rates in order to explore the other device problems associated with high deposition rates. Efforts to reduce the amount of powder formation generally resulted in a loss of deposition rate or in poor uniformity of film thickness.

One problem in device fabrication which is exacerbated by increasing the deposition rate is the contamination of the intrinsic layer by residual dopant species which remain in the deposition system after the formation of the p-layer. In a slow deposition, there is more time for these species to be outgassed and flushed from the system so that the bulk of the i-layer does not become contaminated. However, in a 5-minute disilane deposition, a substantial fraction of the intended i-layer can be doped strongly enough to produce a "dead" layer at the front of the cell [9]. Residual dopants can be reduced substantially by careful design of the system, by heating the chamber walls, and by procedures such as pumping or flushing the chamber for a long time between the p- and n-layer depositions. However, such procedures negate the advantages of high deposition rates. This problem has been overcome by the use of separate chambers for the deposition of intrinsic and doped layers.

#### 1.4 APPROACH

In the present work, a dual-chamber system was used in the fabrication of a large number of solar cells with a variety of deposition conditions. At first, films were deposited from mixtures of disilane and helium at relatively high pressures of 0.5-2.0 Torr. More recently, pure disilane was used at lower pressures of 50-200 mTorr. In both cases, higher power densities than those used for the best silane films were necessary in order to achieve deposition rates of 1.5-2.0 nm s<sup>-1</sup>. Progress was made in achieving high deposition rates without powder generation. Comparisons are made between cells prepared from silane at low rates and those made from disilane at high rates. The results suggest that the defect density in the intrinsic material made from disilane is still a fundamental limitation to making high efficiency cells at high rates. This defect density increases with rf power density, and may be the result of ion damage.

## SECTION 2.0

### EXPERIMENTAL DETAILS

#### 2.1 DEPOSITION SYSTEM

The dual-chamber glow-discharge deposition system shown in Figure 2-1 has been described in detail elsewhere [10]. Each chamber is a 15-cm diameter 6-way cross with a pumping port at the back, a window at the front, an rf feedthrough to the cathode at the bottom, and grounded 10-cm diameter anode at the top. The heater and thermocouple are outside the vacuum space. The electrode spacing is adjustable, but is always 2.5 cm unless specified otherwise. Substrates covering an area 5 cm x 5 cm are attached to an Al slider by a stainless steel mask and transferred between chambers using a magnetically coupled linear-rotary manipulator. The system allows the fabrication of a complete p-i-n structure in either a single chamber mode or a dual chamber mode. The system was constructed using UHV components sealed with copper gaskets throughout except for one viton o-ring at the top of each chamber.

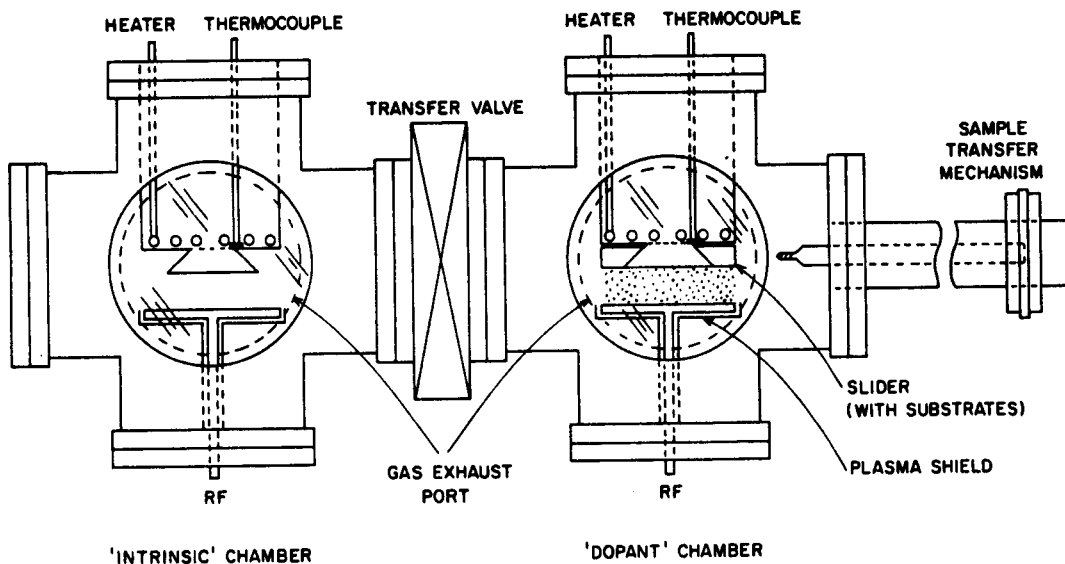


Figure 2-1. Dual-Chamber Glow Discharge System

This design has essentially eliminated the multitude of problems previously experienced with air and water leaks in the Plasma-Therm system. More than 500 depositions of amorphous thin films and devices have been carried out using this unique apparatus. The mechanism for transfer of substrates between the chambers was thoroughly tested and improved until it was highly reliable. The gas-handling system was expanded from 9 to 12 channels, allowing films to be prepared with a wide range of composition. It was found that if the transfer valve was opened when both chambers were evacuated to  $10^{-6}$  Torr, a pulse of trapped gas was released from a virtual leak, threatening to oxidize any fresh film about to be transferred between the chambers. The procedure followed for devices was therefore to flow silane through both chambers during the transfer so that any air released would react with the silane and the products would be carried away before they reached the film surface.

Excitation of the discharge was achieved using a 50 watt solid state rf generator (Amplifier Research) operating at 13.56 MHz, and matched to the load by a Heathkit antenna matching network. Power levels and standing wave ratios were measured with a Micronta SWR meter, and a coaxial switch was used to select the chamber to be energized.

## 2.2 SUBSTRATES

The substrates were pairs of Corning 7059 glass 5 cm x 2.5 cm slides obtained from Cherry Display Products coated with a granular tin oxide having a sheet resistance of 30 ohms/square and a fine-grained texture which assisted in trapping light in the cells by randomizing the internal reflections. Surface temperatures  $T_s$  were calibrated relative to the temperature controller thermocouple using a platinum thin film resistance thermometer pressed against the tin oxide with gases flowing at the deposition pressure, but without igniting a discharge. Actual growth temperatures may be somewhat higher because of heating of the surface by the plasma, but this effect is expected to be small for applied rf power in the range 5-10 W.

## 2.3 GAS ANALYSIS

Measurements were made of the concentrations of volatile impurities in  $\text{SiH}_4$  (Matheson, Liquid Carbonic, Chronar, Scientific Gas Products),  $\text{Si}_2\text{H}_6$  (Matheson, Air Products and Chemicals, Synthatron), and in  $\text{GeH}_4$  (Chronar). As a result of these measurements, and from results obtained in previous years, several conclusions can be drawn regarding the purity of  $\text{SiH}_4$  and  $\text{Si}_2\text{H}_6$  now available. The concentration of volatile impurities in  $\text{SiH}_4$  from several sources is less than 1 ppm and is undetectable with the present BNL modulated beam mass spectrometer system. In  $\text{Si}_2\text{H}_6$ , oxysilanes such as  $\text{Si}_2\text{H}_5\text{OSi}_2\text{H}_5$  and  $\text{Si}_2\text{H}_5\text{OSiH}_3$  are present at low levels, generally <100 ppm. Disilane from Mitsui Toatsu (Air Products and Chemicals, U.S. Distributor) was shown by several investigators to contain ethylsilane,  $\text{C}_2\text{H}_5\text{SiH}_3$ . Recently, a sample of  $\text{Si}_2\text{H}_6$  from Toagosei (distributed by Synthatron) was found to exhibit no detectable oxysilanes. The  $\text{GeH}_4$  contained  $\text{Ge}_2\text{H}_6$  and an unidentified oxygen germane at low levels (190 ppm).

Several methods for analysing  $\text{SiH}_4$  and  $\text{Si}_2\text{H}_6$  with sub-ppm sensitivity were surveyed during the period covered by this report. These approaches included Fourier Transform Mass Spectrometry (FT-MS) and Atomic Absorption (AA) or Inductively Coupled Plasma (ICP) methods. It was discovered that FT-MS suffers from slight changes in the tuning and operation of the instrument that can lead to enormous errors in the measured concentrations. For example, peak height ratios of 1:10 or 10:1 can be observed for two species which are close in mass and abundance, such as  $^{79}\text{Br}$  and  $^{81}\text{Br}$  (isotopic abundances 50.5:49.5). Thus FT-MS is unsuitable at present for quantitative analysis. Present AA and ICP methods utilize a submicron filter material to collect contaminants and concentrate them before an indirect analysis is performed on the digested filter material. There is a wide variability in the chemical affinity of each contaminant towards a each type of filter material, and calibration standards for indirect AA and ICP techniques are difficult to obtain. In short, there is a critical need for the development of gas phase, direct injection AA or ICP techniques, which are unavailable at present.

## 2.4 INTRINSIC LAYERS

In the first 12 months of this period, intrinsic layers of cells were deposited at  $1.5 - 1.7 \text{ nm s}^{-1}$  using 10% disilane diluted in He, at a total pressure of 0.5-2.0 Torr. These conditions produced highly photoconductive layers with low defect densities at the anode [10], but also generated a thick layer of polysilane powder at the cathode. Attempts to eliminate this powder by varying pressure, power and flow rates were not successful, because of either reduced deposition rates or non-uniform film thickness [9]. In the last six months, a different range of conditions (similar to those in ref. 4) was explored, using pure disilane at lower pressures. Film thicknesses were measured at several points using a Sloan Dektak profilometer.

## 2.5 DEVICES

Complete  $\text{SnO}_2/\text{p-i-n}/\text{Al}$  devices were fabricated in order to evaluate each set of deposition conditions. The Al contacts were evaporated using a mask producing an array of circular pads with areas of 0.021 or 0.124  $\text{cm}^2$ , or square pads of area 0.25  $\text{cm}^2$ . Current-voltage curves were measured under simulated AM1.5 global illumination using a Xenon arc lamp with Oriel solar filters calibrated by means of a Hamamatsu photodiode. The calibration was checked by sending a few cells to SERI for measurement. Nevertheless, absolute measurements of efficiency are subject to a number of experimental errors, and should not be taken too seriously. The conclusions in this work are based as much as possible on comparisons of several cells of equal size measured under the same illumination.

## SECTION 3.0

### RESULTS AND DISCUSSION

#### 3.1 INTRINSIC LAYERS

##### 3.1.1 Disilane-Helium Mixtures: Uniformity

Undoped layers were deposited individually on glass substrates in order to obtain a uniformly thick film with low defect density at a high deposition rate (1.5 nm/s). The disilane was diluted to a 10 % mixture in helium in order to reduce the amount of powder formed by gas phase polymerization. It was found that at 1 Torr pressure and 1.25 cm electrode spacing the films covering an area 5 cm x 5 cm were non-uniform with concentric contours (see Ref. [9]). At the center, some films were less than half as thick as at their edges. This pattern was associated with a higher intensity discharge near the circumference of the electrodes. This intense region seems to be a standing wave in the plasma, whose wavelength is dependent on the density of free electrons. Thus the pattern can be altered by changing the total pressure, the rf power density, the gas mixture or the electrode spacing. Increasing the electrode spacing to 2.5 cm (with 1 Torr pressure) or increasing the pressure to 2 Torr (with 1.25 cm spacing) produced highly uniform films at high deposition rates. The wider spacing and lower pressure were chosen for early device fabrication because the amount of powder produced was less in this case.

In attempts to reduce the pressure even further (0.5 Torr) the size of the cathode was changed to determine the effect on uniformity. It was found that when the cathode diameter was 5 cm with the anode diameter fixed at 10 cm the profile of nonuniformity reversed itself, with the center of the film becoming the thickest region. Thus it may be possible to find an intermediate size of cathode which yields uniform films. However, this method may not be scalable to large systems which would be used in industrial production, and is not as easy to accomplish as an adjustment of other process variables.

##### 3.1.2 Disilane-Helium Mixtures: The Powder Problem

The elimination of powder formation under high deposition rate conditions is an important problem. When powder is produced in addition to a film, the process gas is consumed inefficiently. Also, a few grains of powder may become electrically charged and stick loosely to the substrate, leading to pinholes in devices. The placement of the substrates on the upper electrodes reduces this problem the point where small devices can be fabricated without gross defects, but the yield of larger devices is not likely to be good if large amounts of powder are generated. Additional experiments were carried out to search for conditions where no powder was formed. Further dilution of the disilane to 5% in helium caused a significant reduction in powder, which accumulated only in a narrow crescent at the back of the lower electrode rather than covering it entirely. However, the deposition rate was reduced and the film produced was non-uniform. Thus it appears that the important

parameter affecting uniformity and growth rate is the partial pressure of disilane, not the total pressure.

Injecting the process gases as a thin, high-velocity sheet by means of a flat quartz nozzle helped to prevent powder formation in the vicinity of the electrodes, but led to a different kind of non-uniformity. Instead of concentric rings, the interference fringes were straight lines perpendicular to the gas flow, with the thinnest part of the film being upstream. This occurs because the rate of supply of fresh gas exceeds the local rate of decomposition into reactive species.

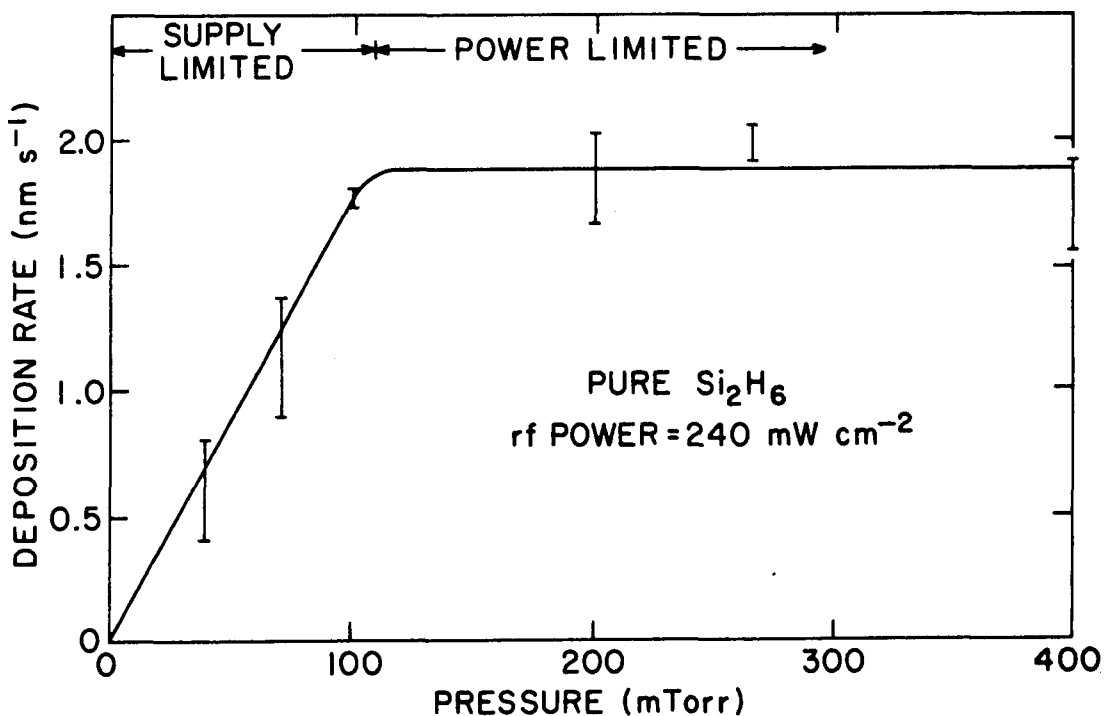
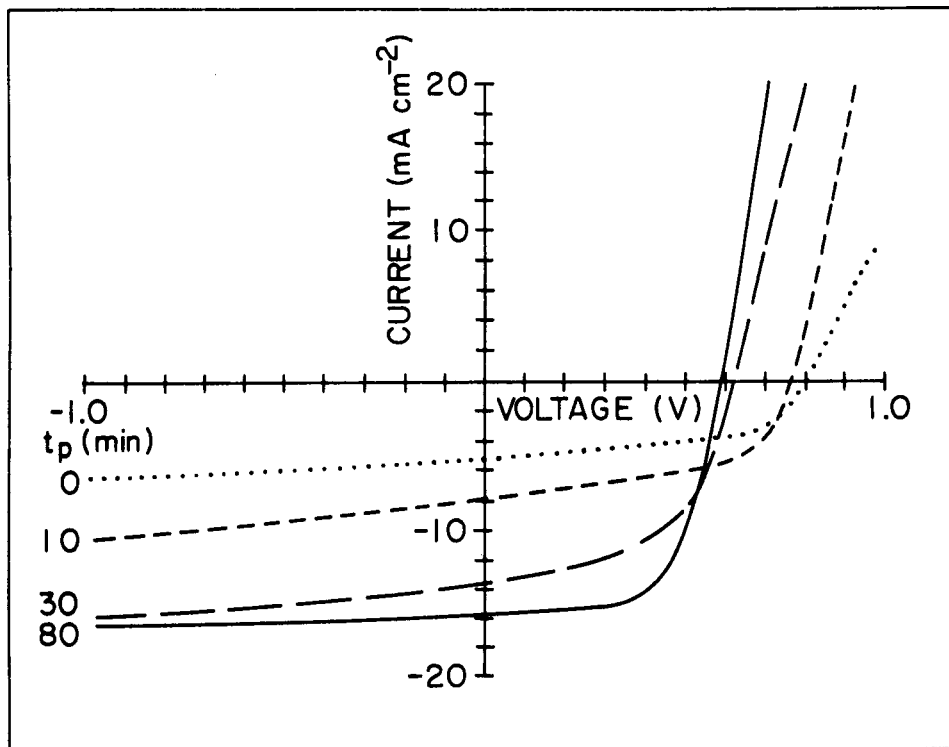


Figure 3-1. Deposition Rate and Uniformity of Films Made From Disilane Discharges at Different Pressures

### 3.1.3 Pure Disilane: Powder Avoided

More recently, a series of films was deposited from pure disilane flowing at 50 sccm using a constant power density of 240 mW cm<sup>-2</sup> (based on cathode size) at various pressures ranging from 40 to 400 mTorr. The deposition rates are shown in Figure 3.1, where the length of the vertical bars indicates the range of deposition rates obtained between the thinnest and thickest measurement points on the substrate (i.e. the uniformity). As others have previously shown for disilane-helium mixtures [7], the curve drawn through these points

can be divided into two regimes. In the supply-limited region the deposition rate is proportional to pressure, and in the power-limited regime the rate is independent of pressure. At the power level used, it was observed that polysilane powder was formed on the cathode only at pressures above the transition point between these regimes. Note that the film grown at a pressure of 100 mTorr not only had the highest deposition rate obtained without powder formation, but also had the best uniformity. This set of conditions was therefore adopted for device fabrication. Devices were also fabricated at lower rates from pure disilane at 100 mTorr using a lower power density of  $120 \text{ mW cm}^{-2}$ .

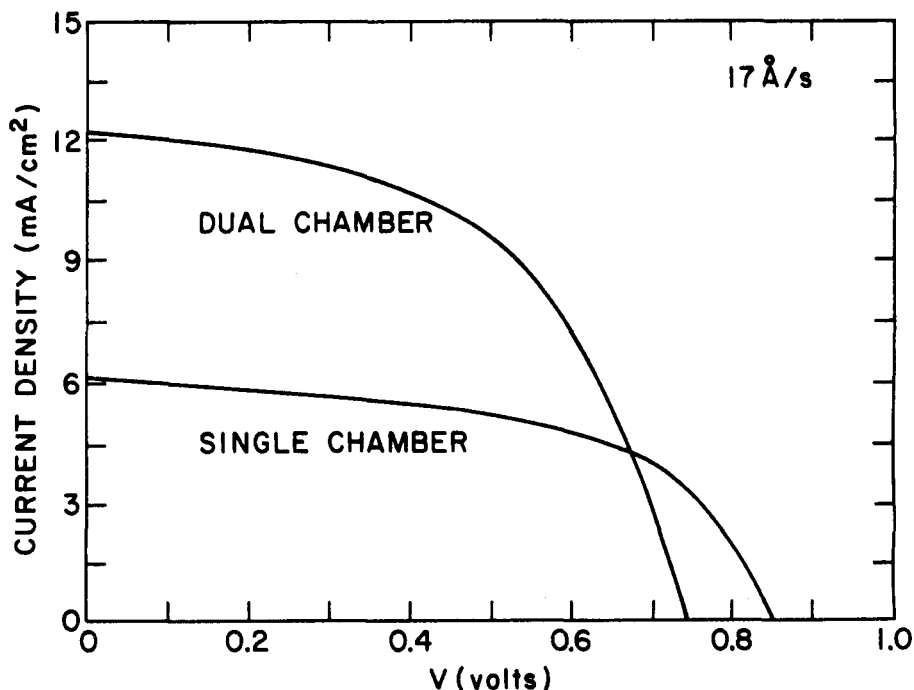


**Figure 3-2. Performance Curves for a Series of Cells Made From Silane in a Single-Chamber System Which Was Pumped Out for a Variable Period  $t_p$  Between p- and i-layer Depositions**

### **3.1.4 Boron Contamination of i-Layers**

The importance of a separated chamber system in fabricating p-i-n cells is demonstrated in Figure 3-2. Current-voltage curves are shown for four cells deposited from silane in a single chamber with p-layers of a-Si:H (no carbon) that are nominally 10 nm thick. The only difference in the growth conditions was the length of time  $t_p$  allowed for diffusion pumping of the chamber between

p- and i-layer depositions. The cell deposited continuously generates a low current, and has a poor fill factor although the open circuit voltage is quite good. As  $t$  is increased to 80 min,  $J_{sc}$  and FF increase substantially, and there is a drop in  $V_{oc}$ . These curves are quite similar to our previously reported comparison of cells deposited from disilane in single- and dual-chamber modes [11], as depicted in Figure 3-3.



**Figure 3-3. Performance Curves for Nominally Similar Cells Deposited in Single- and Dual-Chamber Modes at a High Rate from Disilane**

We attribute both of these results to the effects of boron contamination of the intrinsic layer. After the deposition of a p-type doped layer, the chamber walls and gas manifold surfaces are covered with adsorbed boron-containing species which continue to outgas for a considerable length of time. If the intrinsic layer is deposited immediately, the first part of it will be doped, effectively giving a cell with a very thick p-layer. Since the field in the p-layer is low, this is a dead region where generated carriers recombine rapidly without being collected. Thus the current collected in boron-contaminated cells is low. This problem is eliminated in the dual-chamber mode of operation, where the substrate is transferred to a clean chamber for deposition of the i-layer. For disilane cells grown at high deposition rates, the separated chamber design is essential, because a 1-hour pumping time between layers would defeat the purpose of rapid deposition.

The drop in  $V_{oc}$  which occurs with longer pumping times or with the dual-chamber mode<sup>OC</sup> is interesting, and could have several explanations. First, the abrupt 10 nm thick p-layer may be too thin, and may become slightly depleted of holes [11]. Second, the field near to an abrupt p-layer may be so strong that tunnelling recombination may occur at the junction. Third, an oxide layer may build up during a long pumping period, causing a change in the band-bending by introducing additional defect states [12]. Fourth, the absence of traces of boron in the i-layer may allow the Fermi level to move to an unfavorably high position. Further experiments will be required to determine which of these effects is dominant.

### 3.1.5 Substrate Temperature

A series of cells with a basic p-i-n structure not containing a-SiC was used to investigate the effect of i-layer substrate temperature  $T_s$  on cell performance. The undoped layers of these cells were deposited in the intrinsic chamber of a dual-chamber system with one of three different conditions: (a) pure  $SiH_4$  at low pressure (70 mTorr), (b) pure  $Si_2H_6$  at low pressure (100 mTorr), and (c) 10%  $Si_2H_6$  in  $He$  at high pressure (1 Torr). The deposition rates were 0.1, 1.4 and  $1.7 \text{ nm s}^{-1}$  respectively. The fill factors of these cells are shown in Figure 3-4 and the open circuit voltages are shown in Figure 3-5.

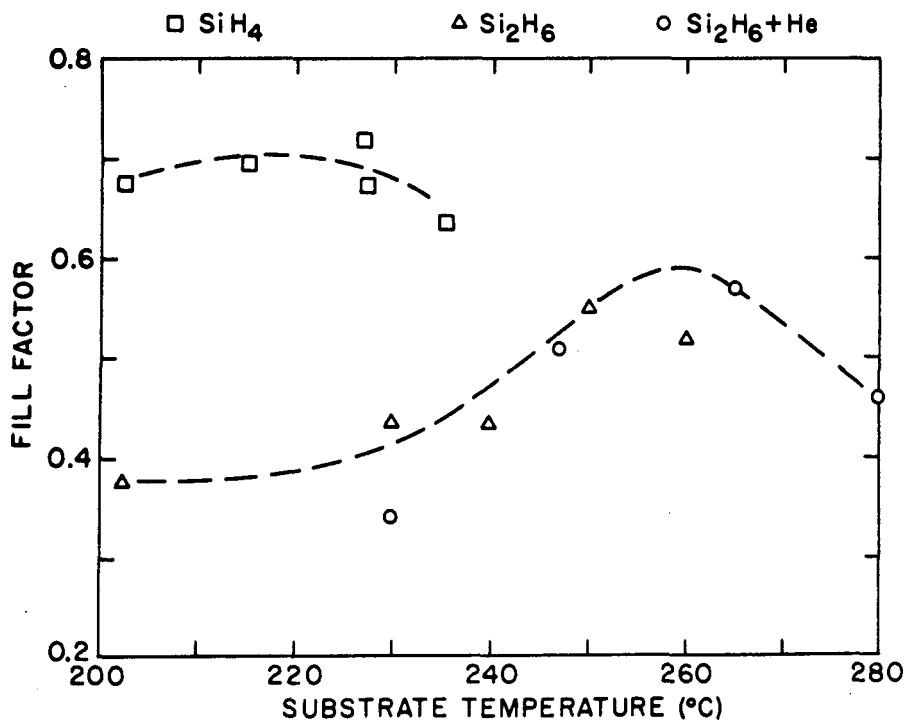
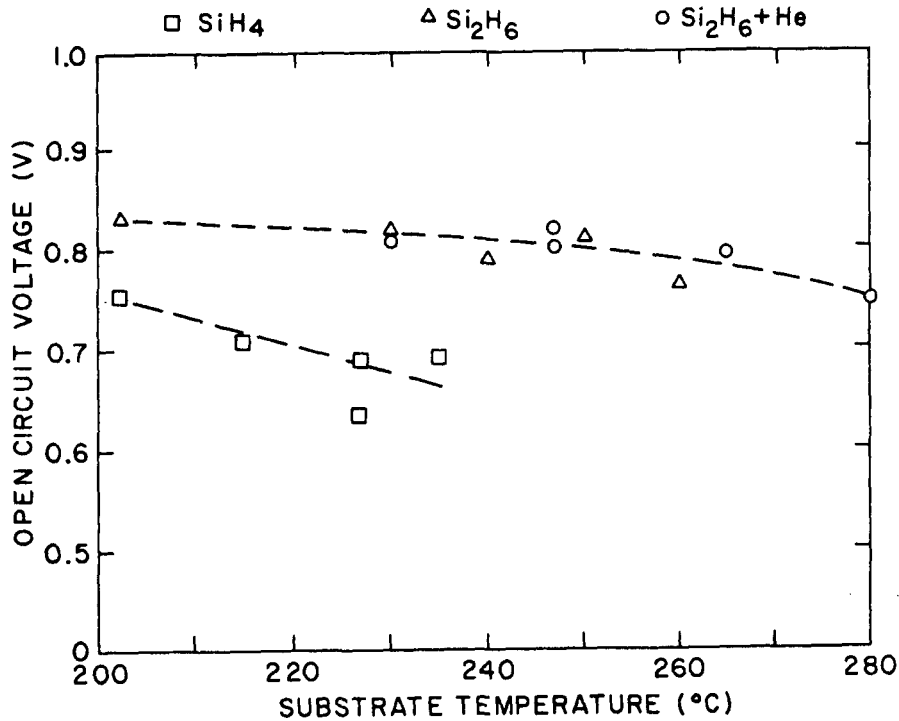


Figure 3-4. Influence of Substrate Temperature on Fill Factors

The two types of disilane cells seem to have similar performances, and similar temperature dependences. However, one should bear in mind that the conditions (c) resulted in considerable gas phase polymerization and powder formation. Conditions (a) and (b) were free of powder.



**Figure 3-5. Influence of Substrate Temperature on Open Circuit Voltage for Silane and Disilane Cells**

One expects the cell parameters to change with  $T_s$  for several reasons. It is well known that the dangling bond spin density has a minimum somewhere in the range 200-300°C. When a cell is forward biased, the internal field is reduced, and carriers become more likely to recombine at dangling bonds than to drift across the i-layer and be collected. The series resistance in the doped layers and contacts, which could affect the fill factor, is constant for this set of cells, so the fill factor is a measure of the defect density in the intrinsic layer [13]. It is interesting to note that the disilane cells are optimized at a significantly higher  $T_s$  and with a narrower peak than the silane cells. This reflects the fact that it is more difficult to eliminate the excess hydrogen from disilane-deposited films during growth. The higher fill factors obtained for cells with silane-deposited i-layers suggest that the defect density is lower in this type of material.

The lower voltages obtained for cells deposited from silane probably are related to the factors mentioned in section 3.1.4. In this case, however, the abrupt junctions are produced by transferring the substrates between chambers rather than by pumping for a long time between depositions. In addition to those effects, the higher voltages of the disilane cells may result in part from the wider band-gap of the intrinsic layers. The band gap and the  $V_{oc}$  both decrease with increasing  $T_s$ .

### 3.2 DOPED LAYERS

#### 3.2.1 Diborane Concentration in Silicon Carbide p-Layers

Using intrinsic layers deposited from disilane at  $T = 250^\circ\text{C}$ , cells were fabricated with a series of different p-layers containing amorphous silicon carbide deposited from methane-silane mixtures. The power level was reduced by a factor of 2 to  $120 \text{ mW cm}^{-2}$ , giving a deposition rate of  $0.6 \text{ nm s}^{-1}$ . The effect of the a-SiC:H is to increase the optical gap of the p-layer, thereby increasing the transmission of light into the active i-layer. The addition of carbon to a-Si:H increases the density of gap states and makes the material more difficult to dope, so the conductivity of the p-layer is decreased.

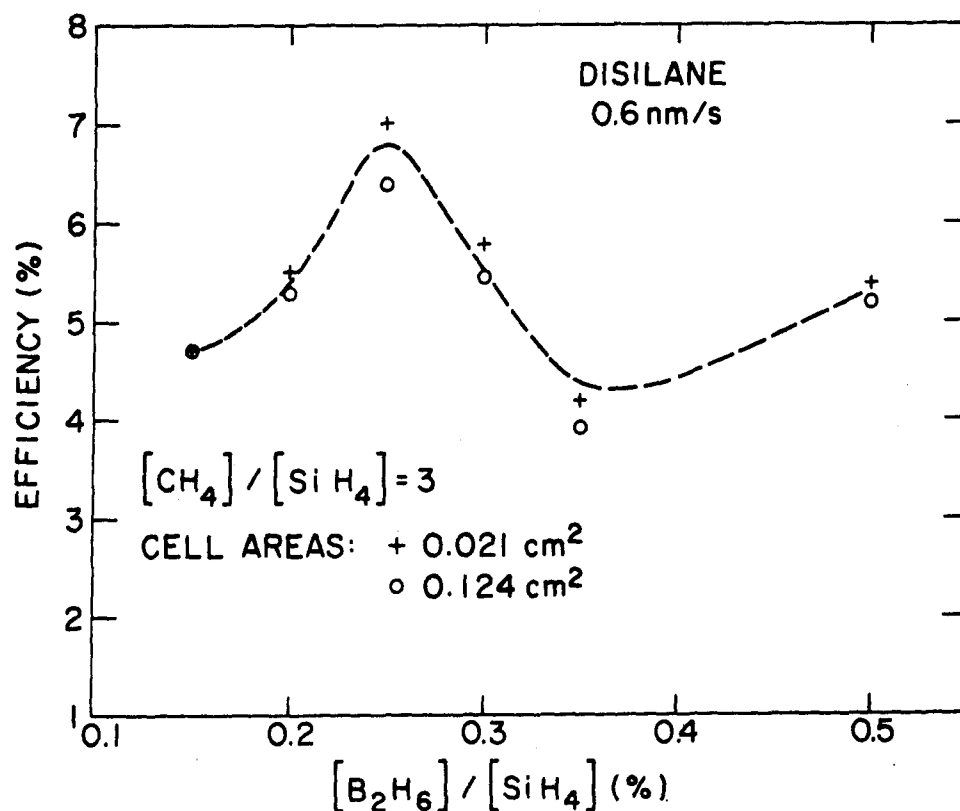


Figure 3-6. Effect of Boron Concentration in p-Layer on Cell Efficiency Using Moderate Deposition Rate

Also, adding boron to a-SiC:H reduces the band gap and increases the optical absorption. It is therefore difficult to predict which gas mixture will lead to the most efficient cell. For disilane i-layers, the performance of the p-layer is crucial, because the absorption in the i-layer is less than in silane i-layers. This is illustrated in Figure 3-6, which shows the conversion efficiencies of this series of cells. A small change in boron concentration seems to cause considerable changes in efficiency. It is possible that the transfer of minute traces of diborane from the dopant chamber to the intrinsic chamber may also be a factor in this result, by adjusting the Fermi level of the i-layer.

### 3.2.2 Amorphous and Microcrystalline n-Layers

Most of the cells made in the period covered by this report contained a 30 nm thick amorphous n-layer deposited from silane containing 0.5 % phosphine. Early results (i.e. from the first 12 months) were obtained using 5 % phosphine diluted in argon, so the discharge contained about 10 % argon. Later, the dopant cylinders were replaced with dopants premixed in silane. The elimination of argon was necessary to reduce the damage caused in the growing film by energetic ions. The connection between argon dilution and high defect densities in intrinsic films has been known for some time [14], and recent experiments with doping-modulated multilayers [15] have indicated that doped films also suffer from the presence of argon during their growth. The thickness and dopant concentration of the n-layer have not yet been varied systematically, because the effects of these parameters are not expected to be as crucial as those of the p-layer.

One variation of the n-layer which was tried a few times was the use of conditions known to give highly conducting microcrystalline films. These films, when grown separately, show less absorption of visible light than amorphous films and much higher conductivities of about  $1-10 \Omega^{-1} \text{ cm}^{-1}$ . It was hoped that their inclusion in cells would raise  $V_{oc}$  by increasing the built-in potential and raise  $J_{sc}$  by reducing the optical absorption. However, no significant improvement was found in the limited number of trial runs made. It seems that the effect of the crystalline regions is not to move the Fermi level higher, but just to move the conduction band lower in the n-type layer. Thus  $V_{oc}$  does not improve. Also, the absorption of infrared light is actually higher in microcrystalline films than in amorphous films, which reduces the part of the generated current which comes from red light reflected off the back contact to make a second pass through the cell. Thus there is no improvement in  $J_{sc}$  either.

### 3.3 COMPARISON OF DISILANE AND SILANE CELLS

Figure 3-7 shows current-voltage characteristics for two cells with essentially the same structure except for the i-layers, which were deposited from silane at  $0.1 \text{ nm s}^{-1}$  in one case and disilane at  $0.6 \text{ nm s}^{-1}$  in the other. The area of each cell was  $0.021 \text{ cm}^2$ . The differences between these cells illustrate the difficulties of using disilane for solar cell fabrication.

Invariably, for a given cell structure, the current generated in a disilane-deposited cell is lower than that obtained with silane. This difference is accounted for by the wider band gap and reduced absorption of red light in the disilane material [10,11]. In addition, the fill factor of disilane cells is usually less than 0.6, whereas we have obtained values of 0.71 with silane. The most likely explanation of this observation is that the density of recombination centers in the disilane i-layers is higher than that in silane i-layers. The open-circuit voltage is similar for these two cells, and seems to be controlled by the a-SiC:H layer rather than by the i-layers as was the case for the cells shown in Figure 3-5. Both types of cell should be improved substantially if better doped layers and interfaces can be developed.

In summary, the best cell made from silane at  $0.1 \text{ nm s}^{-1}$  had an area of  $0.021 \text{ cm}^2$  and an efficiency about 9 %. The best cell of the same area made from pure disilane at a rate of  $0.6 \text{ nm s}^{-1}$  had an efficiency of about 7 %. An earlier cell made from disilane in helium at  $1.7 \text{ nm s}^{-1}$ , originally reported to be 7.3 % efficient based on the mask area of  $0.005 \text{ cm}^2$ , is now estimated to be about 6.5 %, because the Al smears out at the edges of the mask, contacting a larger area. The new conditions permit larger area cells ( $0.25\text{-}1 \text{ cm}^2$ ) to be prepared with a high yield of working devices, but not many have yet been fabricated.

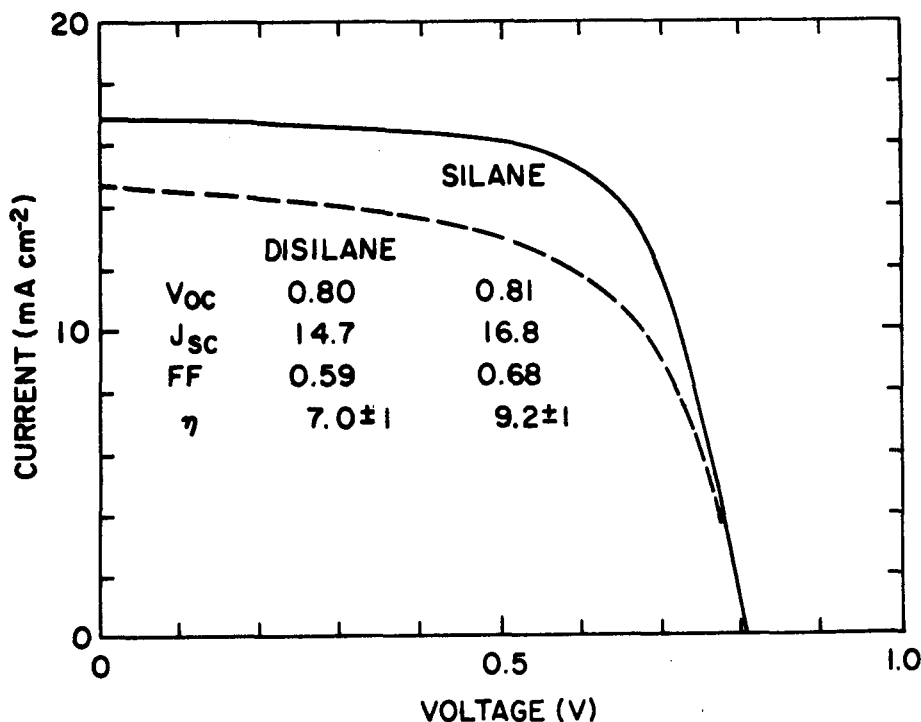


Figure 3-7. Comparison of Disilane-deposited and Silane-deposited Cell Performances

## **SECTION 4.0**

### **CONCLUSIONS**

Fabrication of efficient solar cells at high deposition rates using disilane glow discharges requires very careful system design and process control. The properties of the intrinsic material appear to limit the current and fill factor to values lower than those which are readily obtainable if silane is used at low deposition rate. Further improvements are possible from adjustments of the doped layers and junction regions, which control the open circuit voltage. However, it is questionable whether disilane offers any advantage over silane. Techniques used to improve the disilane cells can also be applied to silane cells, which probably will always be cheaper and more efficient. In this sense, research on disilane cells may still be useful to the industrial development of amorphous silicon devices, but these devices will most likely not be made commercially using disilane.

## SECTION 5.0

### REFERENCES

1. P. E. Vanier, F. J. Kampas, R. R. Corderman, and G. Rajeswaran, Journal of Applied Physics, Vol. 56, 1984, pp. 1812-1820.
2. T. Shimada, N. Nakamura, S. Matsubara, H. Itoh, S. Muramatsu and M. Migitaka, 1st International Photovoltaic Science and Engineering Conference, Kobe, Japan, 1984, pp. 445-448.
3. T. Hamasaki, M. Ueda, A. Chayahara, M. Hirose, and Y. Osaka, Applied Physics Letters, Vol. 44, 1984, pp. 600-602.
4. B. A. Scott, M. H. Brodsky, D. C. Green, P. B. Kirby, R. M. Plecenik, E. E. Simonyi, Applied Physics Letters, Vol. 37, 1980, pp. 725-727.
5. A. Matsuda, T. Kaga, H. Tanaka and K. Tanaka, Journal of Non-Crystalline Solids, Vol. 59&60, 1983, 687-690.
6. A. E. Delahoy, F. J. Kampas, R. R. Corderman, P. E. Vanier, and R. W. Griffith, Proceedings of the 16th IEEE Photovoltaic Specialists Conference, 1982, pp. 1117-1123.
7. M. Konagai, J. Kenne, and Y. Ohashi, Amorphous Subcontractors Review Meeting, Nov.22-24, 1982, pp.1-5.
8. J. Kenne, Y. Ohashi, T. Matsushita, M. Konagai, and K. Takahashi, Journal of Applied Physics, Vol. 55, 1984, pp. 560-564.
9. G. Rajeswaran, P. E. Vanier, R. R. Corderman and F. J. Kampas, Proc. 18th IEEE Photovoltaic Specialists Conference, 1985, pp. 1271-1276.
10. G. Rajeswaran, P. E. Vanier, R. R. Corderman and F. J. Kampas, Proc. Materials Research Society Symposium, Vol. 38, 1985, pp. 394-400.
11. G. Rajeswaran, P. E. Vanier, R. R. Corderman and F. J. Kampas, Proc. Materials Research Society Symposium, Vol. 49, 1985, pp. 27-32.
12. G. Moddel, F.-C. Su, and P. E. Vanier, Proc. Materials Research Society Spring Meeting 1986, Symposium E, Palo Alto (in press)
13. B. W. Faughnan and R. S. Crandall, Applied Physics Letters, Vol. 44, 1984 pp. 537-539.
14. J. A. Reimer, R. W. Vaughan, and J. C. Knights, Physical Review B Vol. 24, 1981, pp. 3360-3370.
15. F.-C. Su, S. Levine, P. E. Vanier and F. J. Kampas, Applied Physics Letters Vol. 47, 1985, pp. 612-614.

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