Device Research Task
(Processing and High-Efficiency Solar Cells)

INTRODUCTION

This task has been expanded since the last 25th PIM to include process research in addition to device research. The objective of this task is to assist the FSA Project in meeting its near- and long-term goals by identifying and implementing research in the areas of device physics, device structures, measurement techniques, material-device interactions, and cell processing.

The research efforts of this task are described and reflect the diversity of device research being conducted. All of the contracts being reported are either completed or near completion and culminate the device research efforts of the FSA Project.

SUMMARY OF PROGRESS

Optimization Methods and Silicon Solar Cell Numerical Models (University of California, Los Angeles)

The goal of this project is the development of an optimization algorithm for use with numerical silicon solar cell models. By coupling an optimization algorithm with a solar cell model, it is possible to simultaneously vary design variables such as impurity concentrations, front-junction depth, back-junction depth, and cell thickness to maximize the predicted cell efficiency.

An optimization algorithm was developed at UCLA and interfaced with the Solar Cell Analysis Program in One Dimension (SCAPID). SCAPID used finite difference methods to solve the differential equations which, along with several relations from the physics of semiconductors, describe mathematically the operation of a solar cell. A major obstacle was that the numerical methods used in SCAPID required a significant amount of computer time, and during an optimization the model is called iteratively until the design variables converge to the values associated with the maximum efficiency. UCLA alleviated this problem by designing an optimization code specifically for use with numerically intensive simulations to reduce the number of times the efficiency had to be calculated to achieve convergence to the optimal solution. Adapting SCAPID so that it could be called iteratively by the optimization code provides another means of reducing the central processing unit time required to complete an optimization. Instead of calculating the entire current-voltage (I-V) curve, as is usually done in SCAPID, only the efficiency was calculated (maximum power voltage and current) and the solution from previous calculations was used to initiate the next solution.

Optimizations were run for a variety of substrate qualities and levels of front- and back-surface passivation. This was done to determine how these variables affect the optimized efficiency and the values of the optimized design variables. The sensitivity of efficiency to each of the design variables was investigated by changing one variable and reoptimizing the others.
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This effort is near completion, and the final work will be to include variables associated with the design of an AR coating in the optimization.

Carrier Transport and Recombination Parameters in Heavily Doped Silicon (Stanford University)

Experimental work on p- and n-type heavily doped layers has been essentially completed. This work has, for the first time, given reliable data of minority carrier diffusivities in both p- and n-type heavily doped silicon, covering a broad range of doping concentrations from $10^{15}$ to $10^{20}$ cm$^{-3}$.

One of the key results is that the minority carrier diffusivities are higher by a factor of 2 in silicon as compared to majority carrier diffusivities. The Stanford University work is written up in their Final Report 957159.

Development and Analysis of Silicon Solar Cells of Near 20% Efficiency (University of Pennsylvania)

The objective of this contract is to identify, develop, and analyze useful techniques for measuring bulk recombination rates, surface recombination rates, and surface recombination velocities in all regions of high-efficiency silicon solar cells. Recent work has addressed the areas of refinement and automation of the previously developed DC measurement "absolute spectral light-beam-induced current" (ASLBIC), and the theoretical evaluation of dynamic measurements in complex device structures.

To make ASLBIC measurements requires UV illumination, especially in "emitters" of high-efficiency solar cells of presently prevailing designs. To improve the ASLBIC measurement accuracy, the system was equipped with blocked interference filters selected to transmit on the various lines of the Hg light source for higher spectral purity. Intensity monitoring, and computer data acquisition and evaluation yielded repeatability of better than half of a percent. For the accurate determination of the absolute light levels, various photodiodes with traceable calibration were used, but systematic calibration differences of 3 to 5% at wavelengths about 400 nm, and greater below 400 nm, were not reconciled. Software was implemented to completely sample the parameter space of the unknown with numerous s,t pairs. The results can be displayed 3-dimensionally showing the full extent of regions of good fit of the modeled to the experimental data. Also, software was written using the simplex minimization algorithm to find the best numerical fit.

A theoretical methodology was developed to analyze and compare the dynamic measurement techniques in existence. In this treatment, the true relaxation constants of the system were identified as sums of the inverse of the bulk lifetime and the eigenvalues of the region where the eigenvalues are a function of the region length, mobility, and boundary transport velocities. It is these relaxation constants that are most directly obtained from dynamic measurements. The relaxation constants were analyzed to determine the relationship to and influence by the complexities of the actual devices. For thin layers, it was
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shown that the eigenvalue term will be large relative to the bulk lifetime term and, hence, will dominate the response. A drift field, as is often present in emitter regions, adds a third term to the relaxation constant. A methodology was developed to calculate the relaxation constants of a compound region such as that present in a base region with a Hi-Lo junction.

This effort has been completed with submission of the Final Report.

SiNᵢ₆ Passivation of Silicon Surfaces (University of Washington)

The primary objective of this program is to investigate experimental techniques for passivating silicon surfaces. The approach consists of: (1) characterization of silicon surfaces of homogeneously doped substrates, (2) surface characterization of high-efficiency n⁺/p and p⁺/n silicon cells, (3) determination of dominant current-loss mechanisms in high-efficiency cells, and (4) physical characterization of interfaces. Special emphasis is being placed on studies of interfaces between silicon and SiNₓ deposited by plasma-enhanced PECVD.

Work has progressed on determining the effect of dopant concentration on surface state density. The approach to investigating this effect was to build metal-insulator semiconductor (MIS) structures and then take high-frequency capacitance voltage (CV) measurements on those structures to determine the interface state density at midgap (Dₛₛ). The MIS structures were fabricated with insulator layers consisting of 700 Å of SiNₓ and were characterized for both n- and p-type substrates. The resistivity of the n- and p-type material varied from 0.005 to 7 ohm-cm, and 0.01 to 7 ohm-cm, respectively.

When high-frequency CV measurements were performed on these structures to determine Dₛₛ, it was found that the SiNₓ/Si interfaces with as-deposited SiNₓ exhibited values of Dₛₛ larger for n-type substrates than for p-type substrates and that, after heat treatment, this difference became even more pronounced. Also, it was found that the Dₛₛ for SiNₓ/n-type silicon is essentially independent of dopant concentration while the Dₛₛ for SiNₓ/p-type silicon interface increases from 10¹² to 10¹³ states cm⁻² eV⁻¹ as the phosphorus concentration increases from 10¹⁶ to 10¹⁸ atoms cm⁻³. These results suggest that SiNₓ can passivate a p⁺/n cell more effectively than an n⁺/p cell.

This contract is near completion and the remaining effort will focus on verifying the passivation results with more testing. Working on special structures also will allow measurement of both surface recombination velocity and interface state density.

High-Efficiency Cell Floating Emitter Design (ASEC)

The ASEC effort during this report period was to fabricate several cell lots (including a final lot) of the floating-emitter design by C. T. Sah Associates. Although the emitter design has several variations, only the back-surface contact (BSC) vertical-floating emitter (VFE) solar-cell transistor (SCT) design was fabricated.
Performance results of the fabricated cells from initial lots were not good. Cell efficiencies of initial lots ranged from 1 to 11% with the majority of cells being under 7%. The $V_{OC}$'s were very good. More than 600 mV in many cases, and up to a maximum of 621 mV. However, the $I_{SC}$'s were not good and accounted for the overall poor cell performances. $I_{SC}$'s were in the 15 to 25 mA/cm² range, some as low as 2 to 3 mA/cm². By comparison, cell efficiencies of the final lot ranged from 11% to more than 15% for an average of 13.2%, with one-third of the cells measuring more than 14% efficient. $V_{OC}$'s ranged from 575 to 605 mV, similar to the previous lots. The best improvement was in the $J_{SC}$ values of the final lot which measured between 35 to 45 mA/cm² for the 4 cm² cells as compared to 2 to 25 mA/cm² for $J_{SC}$'s of the previous lots. It is postulated that those changes from the previous lots to the final lot (that greatly improved current collection efficiency) included reducing the cell thickness from 8 to 4 mils, and increasing the bulk resistivity from <10 to 50 ohm-cm.

Some of the processing problems encountered in fabricating the floating emitter cells included mask alignments, oxide layers, induced during boron diffusion, nonuniformity of both the POC1₃ diffused layers, and the passivated SiO₂ layers. Some of these problems no doubt contributed to some of the poor performances of some cells. The issue that was not resolved was whether or not the floating emitter design is a viable solar cell design, as it was not determined what effect the processing problems had on the overall cell performance. The improvement in performance of the final lot of cells was encouraging and suggested that there might be a potential for the design to be a high-efficiency device. It was concluded, therefore, that the floating emitter design needs more work both in analysis and processing before its full potential as a high-efficiency device can be determined. The ASEC effort is described in their Final Report 957098, which is being completed.

High-Efficiency Solar Cells on Web (Westinghouse)

The major efforts of the Westinghouse contract are to identify carrier loss mechanisms, design high-efficiency cell structures with the aid of numerical models, and to process high-efficiency solar cell structures. The program goal is to produce an 18% efficient dendritic web cell.

Transmission electron microscopy (TEM), laser-beam-induced current (LBIC), and deep-level transient spectroscopy (DLTS) were analysis tools used to compare baseline high efficiency (~15%) with low-efficiency (~10%) web solar cells. The results of these analyses indicated that dislocations (and not twin planes) were the primary causes in limiting diffusion lengths (and, hence, cell efficiency).

It was found that the diffusion lengths and efficiencies of web cells could be improved by hydrogen implantations carried out with an energy of 1500 eV and a beam current density of 2 mA/cm² for 2 min. As an example, the diffusion length (19 µm) and efficiency (8%, no AR) of a cell were improved respectively to 120 µm and 10.3% (no AR) after hydrogen implantation. However, higher quality cells of more than 10% efficiency (no AR) showed little improvement after hydrogen implantation.
A double-layer AR coating consisting of ZnS and MgF₂ was employed to enhance the short-circuit current by 51% and the efficiency by 55%. With this coating and an aluminum BSR, web cells with an efficiency of 16.0% (as measured by JPL) were fabricated.

Final work on this contract included the reduction of the dopant surface concentration and junction depth in the emitter using an arsenic diffusion, and the reduction of base resistivity in the web cell from 4 to 0.2 ohm-cm. With these improvements along with the hydrogen ion implantation, double-layer AR coating, oxide surface passivation, and aluminum BSR, the program goal of an 18% efficient cell may be achieved.

**Laser-Assisted Metallization (Westinghouse)**

The objective of this contract is to develop a laser-assisted metallization process in which the metal grid line pattern is written directly on the cell substrate, thereby precluding the use of photolithography. In its full implementation, there would be no vacuum processing, and a thick (~8 μm) conductor would be electroplated onto the laser-deposited metal in order to carry the photocurrent without excessive ohmic losses.

During this report period, cells were fabricated using an argon ion laser with output power ranging from 1 to 8 W. Initial results (decomposing silver neodecanoate on base silicon) were unsuccessful because the decomposed film would not adhere to the silicon through the subsequent plating processes. To circumvent this problem, 1500 Å of Ti and 500 Å of Pd were first evaporated onto the silicon surface. Titanium provides adherence to the silicon while the palladium cap protects the titanium from oxidation. The silver neodecanoate solution was then spun on the palladium layer, and the grid lines were written with the laser. After rinsing the undecomposed film from the wafer, the grid lines were electroplated with silver. This silver film then acted as an etching mask to remove the palladium and titanium layers from the field.

Cells fabricated in this manner had efficiencies as high as 16.6% with normal fill factors (FFs). The laser processing did not degrade junction quality, bulk lifetime, series resistance, or shunt resistance. However, the necessity of incorporating layers deposited by evaporation detracted from the original goals of this technique.

Several experiments were conducted to incorporate the use of titanium organometallic inks to eliminate the evaporative step. Grid lines were written on spun-on Ti MOD films, which were hard baked at 400°C prior to spinning on the silver neodecanoate. After laser writing, the grid lines were sharp while the remainder of the film had a consistent TiO₂ AR coating. Although the grid lines survived the plating process, their adhesion was unacceptable.

Research on this Ti process was initiated (as well as those using metallo-organic solutions containing adhesion promoters (Bi) or metal ions which are able to form silicides (Ni and Pt)), but was stopped when the follow-on contract was terminated prematurely.
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Ink-Jet Printer System (Purdue University)

The objective of this contract is to develop a computer-controlled ink-jet printer that will print metal inks in a configured pattern on solar cells. The ink-jet printing system uses a modified Siemens print head with 12 nozzles, and a computer-controlled X-Y table upon which the cells to be metallized are mounted. Work since the last PIN has consisted of upgrading the hardware and conducting ink-jet printing studies to evaluate the entire printing system.

The most significant hardware improvement has been the incorporation of an IBM/AT computer to operate the ink-jet printer system. Prior to this, the ink-jet printer system was connected to the Purdue mainframe computer for operation. With acquisition of the IBM/AT computer, the ink-jet printer system is now an independent, standalone, operational system.

The ink-jet printing studies have uncovered a contact resistance problem. It was determined that a silicon oxide layer is formed between the silicon surface and the contacts (metal inks) when the printed ink is fired to remove organics. One approach to this problem is to find an additive for the metallo-organic ink that will form a conductive glass with the silicon oxides during the firing cycle. A second approach is to adjust the firing conditions to eliminate or reduce the formation of silicon oxides. Both approaches are being investigated. Solving the high-contact resistance problem is the last remaining problem to be solved on this contract. The ink-jet printer assembly has been exercised repeatedly and performs well.

Process Research of Non-Cz Silicon Material (Westinghouse)

The goals of the contract were: (1) to investigate simultaneous diffusion of liquid dopants for front and back junctions, (2) to investigate process control parameters, and (3) to perform a cost analysis of the simultaneous junction formation process.

The efforts on this contract end on a positive note. A successful, simultaneous junction formation process using liquid dopants was achieved using a flash diffusion (heat lamp) technique. Earlier attempts to simultaneously form junctions by thermal diffusion of liquid dopants were unsuccessful because of the cross-contamination of dopants on the front and back junctions. The flash diffusion process involves subjecting of the web material to a high temperature, short-time heat pulse from tungsten-halogen flash lamps. Times of 5 to 15 s and temperatures of 1000 to 1150°C were investigated. It was determined that to produce the highest quality cells, an annealing cycle (nominal 800°C for 30 min) should follow the diffusion process to anneal quenched-in defects. Two ohm-cm n-base cells were fabricated with efficiencies greater than 15% (AM-1, 100 mW/cm²).

A cost analysis was conducted using IPEG methodology. The analysis indicated that a cost reduction of 25 to 35% could be achieved when comparing the flash diffusion process to the old sequential diffusion process.
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Rapid Thermal Processing Effects on Cz Silicon Substrates: Defects, Denuded Zones, and Minority Carrier Lifetime (North Carolina State University)

The main objectives of this study were to evaluate rapid thermal processing (RTP) as a viable procedure for: (1) Cz substrate modification using high temperature dissolution treatments, and (2) rapid junction activation following ion implantation. The idea behind the first treatment is to dissolve grown-in defects and nucleation sites for oxygen precipitation, while the second process would be done as quickly as possible, e.g., 10 s, to prevent any subsequent defect nucleation or lifetime degrading processes from occurring.

The experimental approach for substrate evaluation used preferential chemical etching and x-ray topography to delineate defects that are subsequently correlated with minority carrier lifetime which, in turn, is determined by a pulsed metal oxide semiconductor (MOS) test device. The x-ray delineation of grown-in defects were enhanced by a lithium decoration procedure performed at temperatures below 450°C, both prior to and after a high-temperature dissolution anneal. Experimental equipment installed and brought up to operational speed during the initial 8 months of this project include a computerized semiconductor measurement system, Model CSM/16, purchased from the Materials Development Corp., which measures both $\tau_f$ and $\tau_r$ via CV, C-t and C-T analyses, and a 15-kW rotating anode x-ray generator, Elliott Model GX-21, capable of either Lang or double-crystal x-ray topography on wafers up to 6 in. in diameter. Silicon wafers examined were as-grown, as well as furnace and RTP annealed with various combinations of 1200, 750, and 1050°C thermal cycles.

Results showed excellent correlation between process-induced defects and $\tau$ values for $\tau_f$ span a range from 100 to 1000 μm, while $\tau_r$ is generally a factor of $10^7$ lower. RTP-induced slip dislocations were initially the main factor in obtaining low $\tau$, but this has recently been corrected with an improved RTP process.

Diffusion Barriers (California Institute of Technology)

The objective of this effort is to investigate amorphous metal alloys as diffusion barriers in silicon metallization schemes. Amorphous W-Zr and W-N alloys have been investigated as diffusion barriers. It was shown that amorphous W-Zr films crystallize at 900°C, which is 200°C higher than for amorphous W-Ni films, but that the films nonetheless react with metallic overlayers at temperatures far below the crystallization temperature. Specifically, it was shown that failures in a Si/W-Zr/Al metallization were dominated by highly localized interactions. However, W-N alloys (crystallization temperature ~600°C) were applied successfully as diffusion barriers in contact structures with Al and Ag overlayers. The thermal stability of the electrical characteristics of shallow n+p junctions was significantly improved by incorporating W-N layers in the contact schemes. It also was shown that deposition parameters have important influences on the performance of W-N thin films as diffusion barriers.
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Use of Low-Energy Hydrogen Ion Implants in High-Efficiency Crystalline Silicon Solar Cells (Pennsylvania State University)

This program explored the use of low-energy hydrogen ion implants in the fabrication of high-efficiency crystalline silicon solar cells. The work established that low-energy hydrogen ion implants can result in hydrogen-caused effects in all three regions of a solar cell, viz, emitter, space charge region, and base. In web, Cz, and FZ material, low-energy hydrogen ion implantation can reduce the surface recombination velocity. Also in web, Cz, and FZ material, hydrogen implants were found to passivate space charge region recombination centers. In web cells, hydrogen implants were also found to passivate the base region. However, similar improvement was not seen for the base region of Cz or FZ cells. In the case of web material, hydrogen is believed to be able to diffuse into the base region where it can passivate structural defects present in web in the base.

In exploring the fundamental interaction of hydrogen with impurities in silicon, it was found (using DLTS) that H⁺ implants can passivate the deep levels resulting from fast diffusing metal impurities (Au, Cr), but not those resulting from slow-diffusing metal impurities (Ti). This suggests that gettering, not some chemical interaction, may be the dominant "passivation" effect in hydrogen's rendering deep levels inactive. Other fundamental work substantiated the recent result of other groups that hydrogen (in this case, implanted hydrogen) can neutralize boron acceptors in silicon. Heating during H⁺ implantation above ~180°C removes this neutralization phenomenon. It also was established that hydrogen implants can alter the diffusion properties of ion implanted boron in silicon; however, this was not found to be the case for ion implanted silicon.

Heavy Doping Effects in High-Efficiency Silicon Solar Cells (University of Florida)

The goal of this contract is to investigate theoretically and experimentally the effects of heavily doped crystalline and polycrystalline silicon upon the conversion efficiency of junction silicon solar cells.

The results are reported of the first direct measurement of the minority electron transit time in a p-type (Si:B) transparent heavily doped layer. The value was obtained by a high-frequency conductance method. From the transit time, values were determined for the minority electron diffusion coefficient D and mobility μ. The new results indicate that the position-averaged D and μ are smaller by a factor 7 than the corresponding majority carrier μ for a layer whose doping concentration ranged from $3 \times 10^{19}$ cm⁻³ to $10^{20}$ cm⁻³ (Reference 1).

Studies were made of the temperature dependence of the emitter saturation current for bipolar devices by varying the surface recombination velocity at the heavily doped emitter surface. From this dependence, a value for the bandgap narrowing was derived that is in better agreement with other determinations than were previous results obtained from the temperature dependence measured on devices with ohmic contacts (Reference 2).
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Analytical solutions were developed for any degree of accuracy for minority-carrier transport in the passivated emitter layer of solar cells. The simplest of these, accurate to within 5% for most emitters, reveals the competing physical mechanisms in a way that benefits the informed and systematic design of solar cells (Reference 3).

A new method has been developed and illustrated that significantly improves the accuracy of lifetime (τ) determined by voltage transients. This method requires only pressure contacts, and thus may be used to determine τ after key processing steps in manufacturing (Reference 4).

Studies of Oxygen- and Carbon-Related Defects in High-Efficiency Silicon Solar Cells (State University of New York at Albany)

Oxygen- and carbon-related defects were studied in silicon, especially as related to high-efficiency silicon solar cells, including gettering of deleterious impurities. Surveys were made of process-induced defects, of lifetime measurement techniques, and of defect aggregates in general. Coordinated experimental and theoretical studies of process-induced defects were carried out. Studies indicate that the vacancy is the likely source of the anomalous oxygen diffusion (observed by Stavola, et al.) confirmed the identification of the (V·O2) and the (V·O2+0i) center, and indicated that defect-enhanced diffusion (such as ion implantation or neutron trasmision doping) can lead to thermal donors, and presumably other impurity complexes. A theory has been developed that describes the electrical behavior of the hierarchy of thermally induced double donors, including a core and an electronically repulsive oxygen-rich region. Identification has been made of the most likely core for the homogeneously nucleated oxygen precipitate as the "ylid," the saddle point for oxygen diffusion stabilized by the presence of two or more additional oxygens. It also was concluded that the precipitation strain energy can also cause the emission of an interstitial leaving as the core the (V·O2) center; two of these emissions will create a (V2·O2) center, a recombination center, thereby destroying the donor. It also was concluded that the likely emitted interstitial is an unbonded silicon O molecule, which is also the likely interstitial involved in high-temperature and oxidation processes, and in supersaturated "excess" oxygen found in as-grown crystals. The first kinetics model which fits all the thermal donor formation data has been developed. Studies of the multioxygen diffusing defects are under way. Studies were made of the gettering of Fe at oxygen surfaces using Rutherford back scattering (RBS), and using electron paramagnetic response (EPR) have found the (Fe·V·O) center, the basic gettering defect.

Metallo-Organic Decomposition Inks (Electrink, Inc.)

This effort investigates the manufacture and evaluation of selected metallo-organic solutions and covers the details of the associated manufacturing processes. Technical support for the development of solution compositions also was used to optimize their use for metallization in PV cells.
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To date, solutions using four different metals and mixtures of solutions of three of these metals have been made. The primary metallization metal compound under investigation is silver neodecanoate. Other ink solutions being investigated include silver neodecanoate with small additions of bismuth or platinum 2-ethylhexanoate which serve to improve adhesion to substrates and resistance to solder leaching. These compounds were dissolved in benzene or xylene. Nickel 2-ethylhexanoate and nickel neodecanoate also were made. Metallo-organic compounds using gold, silicon, titanium, copper, tin, and lead are planned to determine metal film properties such as conductivity, adhesion, and solderability at low cost.

All of the processes used for the metallo-organic compounds were adapted from those developed at Purdue University under the direction of Dr. R. Vest. Interpretation of thermal analysis results has led to a better understanding of the formation as well as the decomposition reactions and, hence, to improvements in the process procedures. In the case of silver neodecanoate and the nickel compounds, it was determined that the reaction pH required careful control to ensure the yield and purity of the product.

The bismuth and platinum compounds tended to precipitate solids from solution on standing, although no solids appeared in bismuth solutions below 5% after several months. Platinum solutions greater than 5% have not been reliably made because of the formation of a black (decomposition product) precipitate.

Precipitates also occurred when small amounts of concentrated solutions of bismuth and/or platinum compounds were added to concentrated (>20%) xylene solutions of silver neodecanoate. Bismuth compound was added at under 0.5% while the platinum compound was less than 1.5% in the silver neodecanoate solution. The mixed metallo-organic solutions provided the hoped-for performance improvements.

Low-Pressure Chemical Vapor Deposition of Polycrystalline Silicon (Jet Propulsion Laboratory)

In the final attempt to reduce surface recombination at the front contacts, the use of a doped polysilicon layer has shown theoretical promise. The low-pressure chemical vapor deposition (LPCVD) system was modified to deposit polycrystalline silicon to allow the investigation to define the controlling process parameters and requirements for producing films for use as an integral portion of the solar cell contact system.

The film depositions used a conventional h-t wall LPCVD reactor with a dual-stage Alcatel rotary pump. Both undoped and in-situ PH₃-doped polysilicon deposition processes were developed and characterized. At the temperatures (610°C) and pressures (320 mTorr) used, the deposition rate of the undoped silane was 110 Å/min. While at a [PH₃]/[SiH₄] concentration of 2.5 x 10⁻², it dropped to 8.3 Å/min.

Structures were fabricated using a [PH₃]/[SiH₄] ratio of 2.5 x 10⁻². The preliminary data are shown below. The data of each run are the average of four devices.
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The data indicate that LPCVD films can form a viable contacting system and the high FFs show there are no series resistance problems.

REFERENCES


