January 2001 • NREL/CP-520-29429

Tenth Workshop on Crystalline Silicon Solar Cell Materials and Processes

A Summary of Discussion Sessions

Editor:
Bhushan Sopori

Prepared by:
Teh Tan, Dick Swanson, Ron Sinton,
and Bhushan Sopori

Workshop held at Copper Mountain Resort
Copper Mountain, Colorado
August 13-16, 2000

National Renewable Energy Laboratory

1617 Cole Boulevard
Golden, Colorado 80401-3393

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Contract No. DE-AC36-99-GO10337

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Printed on paper containing at least 50% wastepaper, including 20% postconsumer waste

Executive Summary

The 10th Workshop on Silicon Solar Cell Materials and Processes was held in Copper Mountain, Colorado, on August 13-16, 2000. The workshop was attended by 85 scientists and engineers from 15 international photovoltaic (PV) companies and 24 research institutions. Review and poster presentations were augmented by discussion sessions to address the recent progress and critical issues in meeting the goals for Si in the PV Industry Roadmap. A proceedings of the papers presented at the workshop was published and given to the workshop attendees.

The theme of the workshop was *Si Photovoltaics: 10 Years of Progress and Opportunities for the Future.* Two special sessions were held: *Advanced Metallization & Interconnections* — covering recent advances in solar cell metallization, printed contacts and interconnections, and addressing new metallization schemes for low-cost cell interconnections; and *Characterization Methods* — addressing the growing need for process monitoring techniques in the PV industry.

Three students received Graduate Student Award checks, each in the amount of $500, with funds contributed by the PV industry.

The following major issues emerged from the discussion sessions:

- Mechanical breakage in the PV industry involves a large fraction, about 5%-10%, of the wafers. This rather low yield is in part the result of using larger and thinner wafers. Therefore, the breakage issue has become more important than the cell efficiency. It was proposed that manufacturers should form a consortium to look at the grown-in stresses and edge microcracking that may contribute to the fragility of wafers during the process sequence. There is an urgent need for some sensitive, nondestructive way for measuring wafer interior stresses and for detecting microcracks.
- The current use of Al screen-printed back-contacts appears to be incompatible with the PV Industry Roadmap requirements. Problems arise from impurities in the paste, the need for a very deep P^+ region for an effective backsurface field, stress and warpage of the wafer (particularly for thin, ~100-µm wafers) resulting from a large metal coverage, and ineffective gettering if the coverage is low. Use of B for the P^+ region can alleviate some of these problems, but may not be as effective for impurity gettering.
- The PV manufacturers who use hydrogen passivation should incorporate the plasma-enhanced chemical vapor deposited (PECVD) nitride for antireflection coating and hydrogenation. This process step can improve cell efficiency by up to 1.5 points. However, reliable high-throughput equipment is not available.
- There is an imminent need to dissolve metallic precipitates to minimize the electrical shunt problem caused by the "bad" regions in wafers. One approach is to significantly lower the metallic impurity content of the substrate much below the solubility values.
- Industry needs equipment for automated, in-line monitoring and testing. There are simply not many tools available to industry. Although many prototype instruments are in use in an R&D mode, these instruments are not yet available in high-volume, in-line configurations. One problem may be that simple R&D instruments seem to have a market of 50-100 units, essentially one to each national laboratory, manufacturer, and university research laboratory with a photovoltaics program. However, at the industry level, perhaps only several dozen instruments are required if they have the high throughput necessary to be in-line. Another

problem is that each manufacturer does its own custom standards and designs. The design and automation of an instrument is difficult because there is no standard wafer size or type. This is a strong disincentive for equipment manufacturers who might provide in-line test equipment for industry. It was suggested that the rapid growth in the industry would result in demand for significant volumes of test equipment, and perhaps we should update equipment manufacturers on the growing prospects for our industry. Europe has set up a Fast In-Line Control research project for developing in-line characterization methods and tools. The United States may either join the European effort, and/or fund (through PV industry) research programs specifically to address the problems related to stresses, PECVD, and hydrogenation.

- In the Wrap-Up Session of the workshop, there was consensus to create four industry/university teams that would address critical research topics in crystalline silicon: (1) replacing screen printed metallization, (2) the developing a low-cost, nonvacuum hydrogenation process, (3) handling thin wafers through fundamental understanding of mechanical properties and their impact on yield, and (4) understanding and mitigating “bad” regions in crystalline silicon.
- The workshop attendees unanimously agreed that the workshop has served well the PV community by promoting the fundamental understanding of industrial processes, forecasting critical issues and research areas, and promoting a climate of openness to facilitate growth of the industry. Holding future workshops was highly recommended. These workshops can address changing needs of the PV community and, as in the past, develop unified approaches to remedy the bottlenecks within PV technologies.

Discussion I: Ten years of progress

Chairpersons: John P. Benner and James A. Rand

The discussion centered around the major changes that have occurred in the commercial solar cell fabrication processing. It was pointed out that PV industry has introduced several cost-cutting process steps that have also led to higher-efficiency devices. The major changes include:

1. *Replacement of ID saw by wire saw for wafering:* Wire sawing has been a blessing to the PV industry. It has led to production of thinner wafers, lower kerf loss, and lower wafer cost. Because wire sawing produces less surface damage, it requires less chemicals and etching time to remove the saw damage.

2. *Replacement of tube furnaces by belt furnaces:* Many PV companies have replaced thermal furnaces for P diffusion (using $POCl_3$ as source materials) with belt furnaces. In the latter case, the diffusion source is either a paste or a spray-on material (such as phosphoric acid). There was an expressed concern for using belt furnace P-diffusion because the cells appeared to be generally inferior to those using tube diffusion. It was argued that this lower quality could be related to (i) formation of typically shallower junctions in the belt furnace and/or (ii) impurity indiffusion from the diffusion source. The paste or source purity should be better quantified and improved.

3. *Al back-surface field (BSF):* Because Al alloying can provide impurity gettering, PV industry prefers use of an Al-BSF. However, the current backside Al processes are not optimized for gettering. There is also a concern regarding the use of Al alloying on thinner wafers because such contacts cause a stress in the wafer with concomitant warping and wafer-breakage problems. Thus, Al back contacts appear to be incompatible with the near-future requirement of the PV Industry Roadmap (of using thin, ~100-µm, Si wafers).

4. *Si_3N_4 anti-reflection coating:* The PV industry has typically used two types of AR coatings—TiO_2 and Si_3N_4. The recent trend is to use PECVD nitride, which offers an added advantage of acting as a source of hydrogen passivation. It is found that in the case of mc-Si, it alone can improve cell efficiency by up to 1.5 points, but reliable equipment and processes are needed.

5. It is clear that there is the need to dissolve metallic precipitates and deal with the electrical shunt problem caused by the “bad” regions in wafers.

Discussion II: Mitigating the effects of impurities and defects on solar cell performance – impact on crystal growth and cell processing

Chairpersons: Michael Stavola and Teh Tan

The discussion covered an entire gamut of defects and impurities in Si. A particular area of concern was the difficulty in gettering precipitated impurities. A summary of the discussion follows:

Metals are introduced into PV-Si during crystal growth from feedstock and from the growth-environment, and during cell fabrication from processing materials and facilities. Metals in Si, either in dissolved or in precipitated forms, are lifetime killers. When in solution, they act as carrier recombination centers of the Shockley-Reed-Hall (SRH) type. As precipitates also, they are prominent carrier recombination centers, but the mechanisms of recombination are not well elucidated. Ti and V cannot be gettered, but their introduction into Si has been avoided. Other transition metals, e.g., Fe, Cu, and Ni, can be gettered with relative ease when in dissolved form. However, when in precipitated form, it is difficult to getter the metals, because the precipitate dissolution rate is low and because each metal may exist in a few different chemical forms, some of which are more stable than others. An example is that Fe precipitates may be in the form of a silicide phase and a silicate phase. There are no data showing that metals may be passivated by hydrogen or any other schemes. Thus, to minimize the adverse impact of metals on cell performance, we may need to clean up the crystal growth and cell fabrication processes. It is not known whether this will be economically feasible.

Point defects, intragrain dislocations, and grain boundaries are present in mc-Si. The point defect species, vacancies and self-interstitials, are SRH centers, but their concentrations are small. However, dislocations can prominently influence the metal precipitation process. In general, only 1/1000 or even 1/10,000 of the dislocation core atoms are electrically active, because dangling bonds of core atoms of straight dislocations are eliminated by bond reconstruction. The active sites consist of kink/jog site atoms for which bond reconstruction cannot be complete, and hence, have dangling bonds. Dislocations constitute metal precipitation sites. Dislocations are generated during crystal growth as a means of releasing the plastic strains/stresses. The grown-in dislocations are difficult to anneal out by a post-growth thermal process. Hence, their density can be (and has been) minimized only by controlling stresses/thermal-gradient during crystal growth. Grain boundaries are present in mc-Si crystals by their nature of being multicrystalline, and their electrical activity can be diminished by hydrogen passivation.

Because of their prominent electrical activity and because of the difficulties in their removal or passivation, there was an enthusiastic discussion (in the form of questions, answers, and debates) about the metallic precipitates. The aspects involved include the precipitate kind, size, density, shape, chemical state, electrical behavior, and electronic structure. It appears that not much is known of the metallic precipitate electronic structures and the mechanisms responsible for their electrical activities in a quantitative sense. Precipitates of a specific metal may be silicides or silicates or a mixture of both, but in general there is insufficient evidence for drawing a definite conclusion. This implies the importance of the mutual interactions of all impurities present in Si.

With a similar total concentration to begin with, precipitates of different metals are different in sizes (ranging from 10 nm to micrometers), shapes (from platelet to spherical), and may or may not be associated with some dislocations generated by the precipitation process. Such phenomena are due to nucleation differences, volume mismatch differences, and the interaction with point-defects/dislocations. Clearly, there is the need to thoroughly characterize the metallic precipitates, which is a great challenge at least in view of the resources presently available.

While thin cells are less sensitive to the lifetime/diffusion-length of the material, it is certainly desirable to reduce the concentrations of metals in the precipitated form. What can be done? Would it be economically feasible to clean up the feedstock, and the crystal growth facility, to lower the metal concentration in as-grown crystal by, say, two orders of magnitude (from $10^{14}/cm^3$ to $10^{12}/cm^3$). Can the cell processing facilities do the same? Why not perform a pre-gettering treatment of wafers at very high temperature, e.g., at 1200^oC? Modeling has shown that such pre-gettering can be very beneficial in dissolving/removing the metallic precipitates. These are some issues that need to be resolved in the near future.

Discussion III: Need for improved characterization methods for the PV industry

Chairpersons: Stephan Shea and Ron Sinton

The following is a list of typical industrial processes for solar cell fabrication. It includes (in parenthesis) the parameter that is currently used for process monitoring.

- Wafer sawing (thickness)
- Damage removal etch (thickness)
- Texturing
- Diffusion (dopant dose, sheet resistance)
- Coinstack plasma etch (visual)
- HF etch (visual)
- Metallization (paste amount, line width)
- AR (thickness and index using a control single-crystal wafer).

The main control-test in a solar cell facility is performed only on the finished cell. Clearly, automated in-line monitoring/testing schemes/equipment are desired. Europe has set up a Fast In-Line Control research project for developing in-line characterization methods and tools. It is not clear whether Japan has a similar program. No such systematic effort exists in the United States. What the United States can do is to: (1) join the European effort; and/or (2) fund (by industry) research programs specifically addressing the problems related to issues such as stresses, PECVD, and hydrogenation.

The discussion quickly turned to the issue of wafer breakage. It was dramatically stated that as long as 10% or more of wafers were broken and littering the production line, few other more subtle production process-control issues seem very important. There seemed broad consensus, from both CZ and ribbon-silicon manufacturers that this was THE issue of the moment. This issue has become more important than the cell efficiency itself. Experience of various manufacturers indicates that:

- Edge cracks are critical. It appears that wafer-edge engineering, in the form of curving and smoothing the edges, will be beneficial for ensuring a damage-free status.
- Wafer handling can also damage the interior of wafers, resulting in breakage "downstream" It is actually better to reject physically unsound wafers prior to cell processing than to have them break later during processing; in the latter case, the equipment must be cleaned.
- Caustic etching can produce brittle edges and stress points. Alternative etching chemistries were recommended.
- The breakage is caused by the use of larger and thinner wafers. Thus, the stress and physical integrity problems of the wafers are now of importance. Consequently, new ways of measuring and monitoring these wafer properties must be found. Additionally, wafers should be individually inspected for integrity prior to cell processing. Thus, some sensitive non-destructive ways for measuring wafer interior stresses should be developed, perhaps some optical methods, e.g., the Shadow Morie method or the IR birefringence method.

At least two instruments exist for detecting microcracks and have potential for use in-line. One is from a spin-off from ZAE-Bayern, in Germany, and works by applying a heat pattern to a wafer and looking for anomalies in the heat distribution with time. The second instrument uses sound to detect microcracks.

It was proposed that manufacturers form a consortium to look at the grown-in stress that may contribute to the fragility of wafers during the process sequence.

Some other issues were also raised during this discussion session. There are simply not very many tools available to industry. Many prototype instruments are in use in an R&D mode, but these instruments are not yet available in high-volume-in-line configurations. The question was asked, "When I have a machine to commercialize for use in production, what is the expected sales volume from industry?" Simple R&D instruments seem to have a market of 50-100 units, essentially one to each national lab, manufacturer, and university research lab with a photovoltaics program. However, at the industry level, perhaps only dozens of instruments are required if they have the high throughput required to be in-line. One problem is that different manufacturers each do their own custom standards and designs. There is no standard wafer size or type to design and automate an instrument to handle. This is a strong disincentive for equipment manufacturers who might provide in-line test equipment for industry. It was suggested that the rapid growth in the industry would result in demand for significant volumes of test equipment, and we should perhaps update equipment manufacturers on the growing prospects for our industry.

Discussion IV: How do we meet the cell efficiency and throughput challenges of the PV Roadmap?

Chairpersons: Jack Hanoka and Doug Ruby

The PV Industry Roadmap suggests a 40-fold increase in productivity and a 10-fold decrease in cost by 2020. The expectation is also that each PV factory will be manufacturing a large output, perhaps exceeding 100 MW/yr. This requires manufacturers to process cells at a rate of 5 to 10 kW/h with high yield and high machine up-time. How do we realize this goal? Some possible approaches include: (1) continuous, highly automated processing, (2) non-contacting methods, (3) no wet chemistry, and (4) no batch or vacuum steps. An example of item (1) will be to extend the present belt furnace for metallization and diffusion processes to conditions much closer to that of the rapid thermal processing schemes, preferably with the use of non-metallic belts. Examples of item (2) can include the replacement of the present screen-printing process by the ink-jet type process, and the current cell-testing schemes (which are all contacting methods) by some rapid, non-contacting methods. Presently, all damage removal and cleaning steps use wet chemicals, which are costly and environmental unfriendly. It will be beneficial if the use of wet chemicals can be eliminated, but this may not be entirely feasible. The present passivation scheme uses PECVD nitride deposition in a vacuum system, which is costly and time consuming. Can this process be replaced by diffusing hydrogen in a belt furnace?

In addition to changes of individual processing steps, it is also important to redesign the whole crystal-growth/cell-processing schemes, to eliminate as much as possible the needed processing steps while simultaneously improving cell efficiency. Two existing examples along this line are the “monolithic module” processing scheme of Evergreen Solar and the “self-doping” processing scheme of EBARA Solar.

To fulfill the goal of the U. S. Industry Roadmap, R&D efforts on a revolutionary scale appear to be needed. Current resources in the United States or even worldwide, allow only evolutionary progress. Thus, the task is truly challenging.

Discussion V: Metallization issues and potential solutions

Chairpersons: Dan Meier and James Gee

The current metallization scheme of screen printing is mediocre at best. However, an extension to that of self-doping is a good step forward. It appears that some still-better methods will be needed. The currently employed interconnect schemes are not sufficient for meeting future throughput needs. The monolithic module assembly approach also appears to be a good advance, but what is to follow? Basic scientific knowledge of the paste chemistry and physics are needed. The currently used solder is unreliable and environmentally unfriendly (because it contains Pb). This issue should be addressed.

Discussion VI: Concerns and opportunities in thin-film Si solar cell R&D

Chairpersons: Bhushan Sopori and Dieter Ast

Topics that led into the discussion include:

- Is the thin-film silicon (TF-Si) solar cell a breakthrough technology?
- Is the commercialization of TF-Si solar cell technology coming soon ?
- What are the performance-limiting factors of the current TF Si cell approaches?
- How thick is a "TF-Si" solar cell – in the ideal case, or is the question even relevant?
- Will TF-Si technology be competitive with other thin-film solar cells, e.g., $CuInSe_2$?

Currently, the TF-Si technology is not commercialized, and it is not known when this will happen. Opinions on whether TF-Si represents a breakthrough technology varies when judged on the basis of cost. Not enough is known to compare TF-Si technology to other TF technologies, e.g., GaAs or $CuInSe_2$.

In view of the availability of layer transfer techniques employing reusable transferring substrates, an interesting suggestion is to use the technique to fabricate (poly) GaAs cells. It was pointed out that if this scheme is to be practical, the transferring substrate must used more than 70 times. Currently, there are no data that show how many times such substrates can be used.

TF-Si technology can benefit from the thin-film-transistor technology already developed for the display industry (e.g., equipment).

Wrap up

The *Workshop on Crystalline Silicon Solar Cell Materials and Processes* finds itself at a critical crossroads. This is because the issues facing the industry have changed over the workshop's ten years of service to the community. During the past decade, the PV industry has grown ten-fold and has become an established player in the global marketplace. The technical issues facing the industry have therefore evolved to reflect this emergence. In the past, there were many interesting scientific and materials issues for which solutions were required to make particular cell technologies achieve acceptable conversion efficiency. Today, the major silicon technologies are all commercialized, and technical concerns can be classified into three major areas: reducing manufacturing cost, increasing manufacturing volume, and increasing cell performance. This is not to imply that there is no important role remaining for research, because the industry has far to go before it can claim a significant role in meeting global energy needs. The decision, therefore, was to use this wrap-up session to conduct a visioning process for the workshop. The desire was to gather as much input as possible from industry, government, and academia on how the workshop can best serve the community in the coming decade. The following is a synopsis of this process and its findings.

Technical Challenges

To start the process, a candidate list of technical challenges was presented and participants were asked to add any topics that they thought worthy. A voting process was then conducted to rank these in importance. Only industry representatives were invited to vote, and each company was allowed three votes. The following table presents the results. Note that there was remarkable unanimity amongst the workshop participants as to the most important issues. Also that it is not necessarily the case that topics receiving no votes are not important or interesting, only that they were not thought to be relevant in the context of the workshop's mission or were of interest to too few companies.

Number	Votes	Topic
1	6	Develop replacement for, or vastly improve, screen-printed metallization.
2	5	Develop low-cost, non-vacuum, hydrogenation technique, and improve understanding of Si_3N_4 hydrogenation.
3	5	Develop methods of handling and processing thin wafers with high yield.
4	5	Develop new emitter technologies such as selective emitters and heterojunction emitters.
5	4	Discover how to neutralize bad regions and shunts.
6	3	Develop back-junction cells.
7	0	Research passivated back contacts
8	0	Develop production-worthy texturing process for multi-crystalline cells.
9	0	Research thin-silicon cells.

Research Working Groups

It was suggested by one participant that a good way to proceed would be to form cross-functional research teams, or working groups, having representatives from industry, academia, and government, to address the above issues. This approach was discussed and generally approved. Topics of interest need to be of broad interest to the crystalline silicon community, and of such a nature that research findings will benefit all participating companies without infringing on particular proprietary interests of any one company. Based on the above rankings, and following some discussion, the following five working groups were proposed.

The conductive paste working group

The current screen-printed metallization process limits cell performance compared to that attainable with vacuum-deposited and lithographically defined metal. This team would work to improve the performance, and reduce the cost of cell metallization. The following areas are potential research topics:

- Increase understanding of how the metal-semiconductor contact works in the case of pastes with a goal to reduce contact resistance and silicon consumption
- Develop new inks with better conductive and rheological properties allowing thinner lines
- Develop non-contact deposition technologies such as ink-jet deposition

Hydrogenation working group

Hydrogenation is now well established as a beneficial process in all multi-crystalline silicon cell designs. At this point, there is no well-established method of hydrogenation that meets long-range cost goals. The purpose of this working group is to research new low-cost methods of hydrogenation and to further the fundamental understanding of how hydrogenation works. Possible topics for research include:

- Improved understanding of the mechanisms behind Si_3N_4 hydrogenation
- Low-cost methods of Si_3N_4 deposition
- Fundamental research on the mechanism of hydrogen passivation.

Mechanical properties and yield working group

There are many benefits to making cells thinner. Specifically, lower-quality material can be used for the same cell performance; less silicon, which is expensive, is required; and ultimately, higher performance is attainable. Experience has not been very encouraging in this regard, however, because of the increased breakage loss as cells get thinner. The goal of this working group is to better understand the breakage mechanisms so that process and equipment designs can be tailored to thin wafers with high yield. Possible topics for research include:

- Breakage mechanisms
- Growth-process impacts
- Wafer-cutting impacts
- Effect of grown-in stress
- Measurement of grown-in stress
- Analysis and detection of microcracks.

Selective emitters working group

Selective emitters can provide significant cell improvements, but to date no such process is in widespread production (with the exception of the laser buried-contact cell). This working group will research new approaches to selective emitters with the goal of finding one or more processes that cost-effectively increase efficiency. Possible topics for research include:

- Alloy emitters
- Heterojunction emitters
- Selective etching
- Self-aligned two-step processes.

Low lifetime region working group

Grown in regions of low lifetime in cast multi-crystalline silicon still result in lower performance from these wafers than in single-crystal silicon. Much progress has been made over the last decade in understanding the nature of these regions, such as the fact that the low lifetime comes from precipitates; however, to date, no cost-effective method of completely eliminating them has been developed. The goal of this working group is to do just that. This will require a close working relationship between crystal growers and cell manufacturers. Possible topics for research include:

- Identification and understanding of the chemical state of precipitates in low lifetime regions
- Diagnostic methods for detecting and characterizing precipitates
- In-line testing for detection of precipitates
- Innovative methods for eliminating precipitates
- Innovative methods for passivating precipitates.

International participation

The marketplace for PV modules is truly global, and most of the companies manufacturing PV modules are multinational corporations. At the same time, there remain many important technical issues facing the crystalline silicon PV industry that need resolution before the next ten-fold expansion can be sustained. This raises the vexing issue of how best to spend the taxpayer dollars collected by individual countries to support and encourage the continued development of this industry—an industry that almost everyone admits is of vital importance to the world's future. Although, this workshop cannot resolve such overarching issues, as a U. S. taxpayer-supported endeavor, the workshop is particularly affected by policy in this regard because the scientific and technical aspects of the industry cross national boundaries.

Today, the fraction of research in PV that resides exclusively in U. S. institutions and companies is very small. Although it may not be politically feasible for one country to support scientific research in another, many governments do aggressively support international cooperation and scientific exchange. The vehicles for this interaction include support of large experimental tools available to all scientists, international forums, international travel expenses, and international fellowships. This workshop will continue to foster an international exchange of science related to PV technologies by actively seeking global participation.

Working-group meetings would be scheduled in conjunction with the three international PV conferences as well as the workshop. This would result in each working group having two meetings per year—a reasonable frequency. As for funding the research activities of each working group and its members, this would be left to traditional methods of proposals to various funding agencies. In fact, for most researchers, the working-group topics would probably represent only a fraction of their research activity.

By acting as the catalyst to nudge research in the directions needed by the crystalline silicon community, and by providing a framework and forum for this research, the workshop will continue to be a central factor in the continued emergence of cost-effective solar power.

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
January 2001

3. REPORT TYPE AND DATES COVERED
Conference Proceedings

4. TITLE AND SUBTITLE
Tenth Workshop on Crystalline Silicon solar Cell Materials and Processes: A Summary of Discussion Sessions, August 13-16, 2000, Copper Mountain, Colorado

5. FUNDING NUMBERS
C:
TA: WO977599

6. AUTHOR(S)
B. Sopori, T. Tan, D. Swanson, R. Sinton

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401-3393

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
NREL/CP-520-29429

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

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14. SUBJECT TERMS
photovoltaics; crystalline silicon; solar cells; materials and processes; impurities and defects; passivation; metallization and interconnections; characterization methods

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRACT
UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102