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14th Workshop on Crystalline Silicon Solar Cells & Modules: Materials and Processes

Summary of Discussion Sessions

Bhushan Sopori, Editor

Prepared by:
T. Tan, R. Sinton, D. Swanson, and B. Sopori

Workshop held at Winter Park Mountain Lodge
Winter Park, Colorado
August 8–11, 2004

National Renewable Energy Laboratory
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The 14th Workshop on Crystalline Silicon Solar Cells and Modules: Materials and Processes

Executive Summary

The 14th Workshop on Crystalline Silicon Solar Cells and Modules: Materials and Processes, was held in Winter Park, Colorado, on August 8 – 11, 2004. Representing many different countries, there were 118 scientists and engineers, from 28 international PV and semiconductor companies and 22 research institutions, participating in this workshop. The theme of the workshop, Crystalline Silicon Solar Cells: Leapfrogging the Barriers, was selected to reflect the astounding progress in Si-PV technology during last three decades, despite a host of barriers and bottlenecks. A combination of oral, poster, and discussion sessions addressed recent advances in crystal growth technology, new cell structures and doping methods, silicon feedstock issues, hydrogen passivation and fire-through metallization, and module issues/reliability. The following oral/discussion sessions were conducted:

- Technology Update
- Defects and Impurities In Si/Discussion
- Rump Session
- Module Issues and Reliability/Discussion
- Silicon Feedstock/Discussion
- Novel Doping, Cells, and Hetero-Structure Designs/Discussion
- Metallization/Silicon Nitride Processing/Discussion
- Hydrogen Passivation/Discussion
- Characterization/Discussion
- Wrap-Up

This year's workshop lasted three and a half days and, for the first time, included a session on Si modules. A rump session was held on the evening of August 8, which addressed efficiency expectations and challenges of c-Si solar cells/modules. Richard King of DOE and Daren Dance of Wright Williams & Kelly (formerly of Sematech) spoke at two of the luncheon sessions.

Eleven students received Graduate Student Awards from funds contributed by the PV Industry.

The workshop addressed funding needs for Si research and for R&D to enhance U.S. PV manufacturing. The wrap-up session specifically addressed topics for the new university silicon program.

SUMMARY OF DISCUSSION SESSIONS

SESSION 3: DEFECTS AND IMPURITIES IN SI

Discussion Leader: Kim Kimerling, Massachusetts Institute of Technology

The discussion leader posted four general topics for discussion:

- Shunt paths—Precipitates and leakage current
- Recombination centers—Solubility, energy levels and capture cross-sections; boron, hydrogen
- Contacts—BSF uniformity, interfacial reactions, stress, morphology
- Coatings—Light trapping

Shunt Paths

Shunting in solar cells typically occurs because of two mechanisms: (1) dislocation clusters decorated by metallic impurity precipitates, and (2) shorts produced by metal punching through the junction, especially in shallow junction cells*. Self-doping pastes for metallization can overcome the punch-through type of shunts by pushing the junction forward. To treat the dislocation/precipitates type of shunts, a general consensus is to use high-temperature gettering together with slow cooling. Only at high temperatures will the metal dissolution process from precipitates be effective, and slow cooling avoids the precipitate re-nucleation problem, which can adversely influence the gettering results. It is desirable and may be possible to avoid the introduction of metals into Si by cleaning up the feedstock.

(*Another reason for shunting has typically been breakage of texture peaks prior to metallization, which subsequently were covered by metallization. Current automation techniques have greatly reduced this failure mechanism.)

Recombination Centers

Carrier recombination in current commercial solar cells is primarily dominated by impurities and defects. As the wafer gets thinner, the dependence of cell efficiency on dissolved impurities becomes less important. It is believed that for a 100-µm-thick cell, a metallic impurity concentration of 10^{14} cm^{-3} can be tolerated. Such a concentration would be too high for current 250-µm-thick wafers. However, if the impurities form precipitates, they can cause junction shunts. It is generally believed that grain boundaries are less harmful than dislocations decorated by metallic precipitates, because the former can seemingly be passivated by hydrogen whereas the latter cannot be. Oxygen, carbon, and nitrogen might be able to hinder dislocation generation. There is the interesting suggestion of self-doping the grain boundaries to become non-recombination regions by repelling the minority carrier away, but it is not known how to do this.

Ga doping improves light degradation in CZ cells but not mc-Si cells.

Hydrogen passivation may need just the right amount of H. Too little may not have much effect, whereas too much may cause hydrogen to form compounds, which would decrease the solubility of dissolved hydrogen and hence its effectiveness. A PECVD nitridation process provides a hydrogen source and the concurrent ion damage to the Si surface absorbs hydrogen, leading to passivation. On the other hand, the LPCVD deposition process does not provide a hydrogen source, and the nitride is a barrier to hydrogen diffusion.

Contacts
Contact formation renders no effect on stress and dislocation generation. We need to improve the uniformity of back contacts, to produce a uniform back surface field, e.g., via RTA.

Coatings
Is today's antireflection coating enough? Lots of light is still lost. Reflection from the wafer backside is only about 20%.

SESSION 4: MODULES AND RELIABILITY

Discussion Leaders: Jack Hanoka, Evergreen Solar
Michael Quintana, Sandia National Laboratories

Planned discussion topics:

- Module considerations for a better cell design
- Thin cell compatibility with current module design

The majority of the discussion was directed to addressing module reliability from a marketability standpoint. Solar panels should be market driven. When buying goods, consumers judge availability, performance, reliability, and cost, all of which are mutually dependent. However, when buying electricity, consumers do not have such choices.

For the next generation of panels, we must improve compatibility with market demands. The main factor is cost. Cost reduction must be through better cell design, better performance, and better packaging. It might not be necessary to further improve the panel reliability (currently set at 20-25 years and expected to extend to 30 years). In the next 5 years, the following improvements can be expected:

	Cost	**Performance**	**Reliability**
Devices	H	H	M
Materials	M	M	M
Packaging	M	L-M	M
Processes	M	M	M

H = probability high; M = probability medium; L = probability low

RUMP SESSION: EFFICIENCY EXPECTATIONS AND CHALLENGES OF c-SI SOLAR CELLS/MODULES

Moderator: Bhushan Sopori, NREL

Panel Members: Mohan Narayanan, BP Solar; Jack Hanoka, Evergreen Solar; Juris Kalejs, RWE Schott Solar; Chandra Khattack, Crystal Systems, Inc.; Dick Swanson, SunPower Corp.; Gerhard Willeke, Fraunhofer, JSE

Planned topics:

- How long will c-Si be the dominant PV technology in the marketplace?
- How thin can Si wafer be?

The session started with some preliminary remarks by the moderator, followed by brief statements by the panelists relating to the discussion topics.

Hanoka: The mc-Si cell efficiency will reach 17% in 5 years, and c-Si will be the dominant PV technology for the next 15-20 years. The challenges are to increase cell efficiency and to reduce cost, which are difficult to achieve at the same time. More specific needs are: developing low-cost equipment, e.g., for hydrogen passivation; reducing dislocations and impurities; better handling of thin wafers; and designing novel modules/cells.

Khattak: c-Si will be the dominant PV technology for a long time to come. The challenges are how to increase efficiency and lower cost simultaneously. We need thin wafers, automated simple module and cell processing, high-yield crystal growth, all at low costs, and low-cost SoG materials.

Narayanan: From 1980 to 2000, there were continuous increases in cell efficiency, wafer size, yield, and installed power output, while the wafer thickness continuously decreased. This trend will last to 2010 and beyond. The enabling factors are cast process improvement, wire sawing, cell processing, and equipment improvement.

Swanson: The empirical c-Si history shows that, from 1980 to 2000, the module cost decreased linearly from $21.83/W to $3.84/W. Extrapolating to 2010, one will have modules at $1.44/W. The reasons for the cost decrease are improvement in cell efficiency. Since the Si theoretical efficiency is 29%, present c-Si cells still have large room for improvement. C-Si solar cell technology has long passed its initial learning stage and is well into the production stage. Entry of a new technology will have to go through a similar learning stage and will not be cost effective during the initial stages of the learning curve. Therefore, c-Si technology will dominate for a long time to come. Besides, there is currently no promising technology that can compete with c-Si.

Kalejs: EFG ribbon material can be thinner. If it can reach an18% efficiency, mc-Si will dominate at least for the next 15 years. However, it will be difficult to handle thin wafer edges in cell processing. The largest hurdle for ribbon material is its small market share in comparison to the other crystalline silicon materials.

Willeke: The c-Si market exceeded earlier predictions, whereas predictions on other technologies did not materialize. In the c-Si market, the mc-Si share has increased while the sc-Si share decreased, but both expanded in terms of installed power. The reason is a continuous decrease in cost brought about by ever increasing efficiency. Any new technology will have to go through the same learning process and, hence, will have a difficulty entering the market.

Sopori's summary:

1. c-Si will dominate in the next 10-20 years.
2. Cell efficiency >17% has already been reported commercially. Higher efficiency is already happening.
3. SoG Si essential. The up graded MG-Si (SoG-Si) is the best solution for feedstock.
4. New ideas/concepts in modules: interconnects, contacts.
5. What is SoG Si? How different is it from micro-electronic-grade Si?
6. The community has a clear view—c-Si will dominate!
7. Any new technology will have difficulty penetrating the existing market of c-Si.

But there are challenges. The industry must:

1. Reduce the cost of equipment
2. Improve wafer handling
3. Increase long-term reliability
4. Improve light trapping in mc-Si.
5. Understand that going thin is not easy, e.g., handling, passivating the surfaces, etc.

General discussions:

(i) Some believe that thin-film Si can catch up with c-Si, but the ideas did not get a warm reception.
(ii) The most promising alternative technology may use the tandem cell structure with a lower cell of c-Si cell and an upper cell of a material of higher-efficiency.
(iii) To meet the challenges, the United States should increase research and development funding for c-Si solar cells.

SESSION 5: SILICON FEEDSTOCK

Discussion Leader: Jim Rand, GE Energy
Panel Members: Vishu Dosaj, Dow Corning; Bart Geerligs, ECN; Elias Macalalad, Solar Grade Silicon; Ragnar Tronstad, ElkemSolar AS; Satoru Wakamatsu, Tokuyama

The discussion focused on how to produce feedstock for SoG-Si.

With regard to solar grade silicon: Will it happen this time? Worldwide demand on Si is outstripping supply. We are living off inventory. Prices are increasing.

Discussion topics:

- Knowledge on impurities has reached an unprecedented level—Is it time to develop new specifications?
- Can the Siemens process fulfill the multi-MW market need?

- Is the industry forced to a single grade Si?
- As efficiency increases, will it play down the cost issue?
- Are we too late?

Macalalad: Solar Grade Silicon, LLC, has completed its development of producing granular Si by a fluid-bed process, and is setting up a 200-ton/Y plant. Will commercialize their product at a price in the low $20/kg range.

Wakamatsu: Tokuyama uses a vapor-liquid-deposition (VLD) method, starting from SiH_4. The material is clumped together particulates that are continuously produced at a high rate. Pilot plant development is completed. Will complete feasibility studies of a 200-ton/Y plant. Will start large-scale commercial plant (1000 ton/Y) by 2008. Material is highly pure, with total metal content of around 100 ppba. The target is in the <10 ppba range.

Geerligs: ECN took the direct route to SoG Si using ultra-pure SiO_2+ C. Uses plasma reactor to remove C. The process has the potential of achieving low cost.

Tronstad: Elkem uses MG Si, which involves the following sequence —slagging/alloying—trapping/solidifying—crushing/sizing—leaching/classifying—refining/casting—sizing QC/QA—SoG Si. Lab-size ingot cell efficiency is 13.4%; targeting for 15% or better.

Dosaj: Dow Corning is a major player in chemical-grade Si (better than MG Si) and is the largest supplier of SG Si. It is two years into development of SoG Si, with a total metal in the <25ppm range. The goal is for B, P, and M all in the <1 ppm range. Expect to have tons by the end of 2004 for evaluations.

Some general points:

Different solar cell Si may need different SoG Si specs. This is technically feasible, but may not be economically feasible for any one SoG Si feedstock supplier. Most SoG Si feedstock suppliers just want to make their Si as clean as possible.

— The Siemens process cannot fulfill all the needs, nor is it desirable.
— Even with cell efficiency increases, Si cost is still a major cost factor.
— It is not yet known how much C can be tolerated in the SoG Si feedstock. 10ppm? 1ppm?
— It is inevitable that SoG Si feedstock for CZ must have a different spec from that for mc-Si.

SESSION 6: NOVEL DOPING, CELLS, AND HETERO-STRUCTURE DESIGNS

(The discussion session was in two parts following each of the split oral sessions)

Part I – Discussion Leader: Steve Shea, Solar Manufacturing Consulting

This discussion followed an earlier presentation on Organic Photovoltaics by Aaron Wadell, Global Photonic Energy Corporation, who introduced it as a "disruptive technology."

How to recognize a disruptive technology?

- PV may be viewed as a global disruptive technology for the power market, if oil prices stay above $40/barrel. However, different solar cells cannot be disruptive to each other, if they compete for the same market.
- Disruptive technology goes for the niche market, e.g., a-Si for consumer electronics.
- Perhaps a true disruptive technology is one that does not rely on the same kind of learning experience as the mainstream technology it is to replace, so that it does not suffer from the very large initial start-up cost while in the meantime offering improved and/or added functions and performances.
- Organic PV has some markets, e.g., for its use on flexible roofs.

Is a-Si coming back to disrupt c-Si? No. It looks like a-Si will have a place in enhancing c-Si cells, as in the hetero-structure cells.

Part II – Discussion Leader: Vijay Yelundur, Georgia Tech

Are n-type Si wafers and n-base cells viable for PV?

- Will we have cells in which low-temperature emitter formation processes (deposited, plasma immersion, etc.) replace P-diffusion?
- Does Ga doping (CZ and mc Si) yield higher stabilized cell efficiency than B-doping?
- Does Ga ingot resistivity variations increase cost?
- Other.

Si and Si cells that are n-type may or may not be a viable alternative. Whereas n-type multicrystalline Si appears to be more tolerant to defects and impurities than p-type, as observed in lifetimes and diffusion lengths. Cells fabricated up to now do not seem to show a definitive higher efficiency. The reason is that the junction shunt resistance is low, leakage current is large, and V_{oc} is low, which is probably caused by the fire-through junction formation process in making contact to the p+ emitter.

One reason for going to n-type is that a large quantity (2000 tons) of scrap n-Si is available. But this is beginning to be depleted.

In early days, n-based cells did not become the mainstream device, because in earlier times (1970s) the availability of n-type Si was a problem. Also, n-based cells are less resistant to radiation damage, and space applications were the main driver at the time.

If oxygen is low in concentration, n-cell is not necessarily more resistant to LID than a p-cell.

Ga ingot resistivity probably will increase the cost.

SESSION 7: METALLIZATION/SILICON NITRIDE PROCESSING

Discussion Leader: Jalal Salami, Ferro Corporation

Discussion topics: Fire-through metallization
Effect of SiN:H thickness on fire-through contacts

Fundamental research of fire-through mechanisms

- Glass chemistry
- Optimizing contact firing
  - Effect of SiN:H thickness and index variation
  - Single step vs. multi-step firing
  - Printing
- Improved metallurgy
  - Lead-free platform
  - Lead-free back silver
  - Lead-free front contact
  - Thin wafers
    - Low bow lead-free Al paste
    - Hot melt paste: reduce handling, high aspect ratio metallurgy
  - Low-temperature firing paste?
  - High sheet resistance (70-100 ohm-cm) textured wafers?
  - Printing vs…..?

Firing through of Ag paste is important for shallow emitters with high sheet resistance- one must be careful not to shunt the junction.

Frit ("eats" through SiN) chemistry is important, but is not understood.
Is doing metallurgy before AR coating a viable alternative?
A fire-through method for p-type contact?
Develop a frit that attacks SiN but not Si?
Losing V_{oc} might be due to loss of H.
Can the paste be cheaper?

Using Cu metallurgy is not an alternative for cheap solar cells. Cu needs to be isolated by diffusion barriers, for which the cost will be quite high.

There is some un-reacted glass surrounding silver particles. This increases contact resistance, but it may also provide adhesion for the particles contacting Si.

Much of the characterization of firing processes uses V_{oc} and FF as a measure of performance. A better set of parameters would be the V_{oc} at $1/10^{th}$ sun, or the dark voltage at $1/10^{th}$ J_{sc}, since this voltage is close to the V_{mp} and is very sensitive to shunting and recombination effects at the maximum power point. V_{oc} at one sun is not very sensitive to shunting effects.

SESSION 8: HYDROGEN PASSIVATION

Discussion Leader: Bhushan Sopori, NREL
Panel Members: Mike Stavola, Lehigh University
Juris Kalejs, RWE Schott Solar
Giso Hahn, University of Konstanz

Discussion Topics:

What is being passivated?
Does fire-through process maximize impurity/defect passivation?
Surface passivation
SiN:H composition vs. passivation

It is obvious that H passivates defects and impurities, but no details are known. It is known that H ties up dangling bonds and thus removes levels from the gap, e.g., at metal-precipitate-decorated dislocations.

For the PECVD SiN:H process, Si surface is damaged (probably in the form of plate type bubbles containing H_2) and serves as a source of H. However, some believe that HWCVD does not cause damage (?) but perhaps yields Si-rich, SiN:H.

There seems to be reason to believe that we do not know how H diffuses through the n+ region.

The fire-through process is a single step serving three functions: to form BSF, to form front contact, and to passivate the bulk. Optimization for passivation requires lower temperature. For the present paste, this is done at about 800 °C for the formation of good front contact. If appropriate paste is available, this temperature may be lowered.

Surface passivation seems to become better after fire-through.

Will stress influence H diffusion? Probably not.

SiN:H composition does influence passivation. It seems to be optimized at a lean NH_4-to-SiH_4 ratio, i.e., for a Si-rich SiN:H film.

SESSION 9: CHARACTERIZATION

Discussion Leader: Dieter Schroder**,** Arizona State University

In general, it is desirable to characterize material and cells as little as possible.

- For materials, want to measure/characterize (1) impurity, (2) resistivity, (3) stress, and (4) structure.
- For impurities: μWPCD, SPV, PL, FTIR (O, C, H, N), TXRF, SIMS, TOF-SIMS, ICP-MS, EBIC, LBIC, XBIC, XRF, EDS, DLTS, neutron-activation.

Cheaper tools are becoming available.

- For resistivity: 4-point probe (Hg 4-point probe), eddy current (QSSPC)

Still no automated 4-point/ Hg-4-point probes.

- For stress: Raman, acoustic vibrations, optical polariscopy, IR transmission

Not routinely measured by PV industry. Not needed, only interested in avoiding wafer breakage, and diagnosing cracks, etc. An optical means for doing this is on the way.

- For structure: ellipsometry, reflectance, SEM, TEM, AFM.
- For cells, wants to measure/characterize (1) efficiency, (2) impurities, (3) sheet resistance, and (4) contacts.
- Contact mapping tool is becoming available.
- How much inline control and how many diagnostic tools can the industry afford? A guideline is that it should reduce the cost due to the realized benefits.
- No inline junction-depth and surface concentration measurement tools yet.
- Measurements/diagnoses can improve PECVD machine utilities, e.g., by providing data for adjusting operation parameters. Need in-situ capability to do this.

WRAP-UP

Moderators: Dick Swanson, SunPower Corporation and Ron Sinton, Sinton Consulting

Topics:

1. 14^{th} Workshop Assessment: good and bad
2. Inputs for 15^{th} Workshop
3. Input for NREL University Initiative
4. Input for DOE White Paper

Good and bad aspects of the organization of the 14^{th} Workshop and suggestions for the 15^{th}.

There was general consensus that the new schedule starting on Sunday morning worked very well. The Saturday-night stay gave low-cost flights, and this allowed for more breaks in the schedule. Having part of Monday afternoon available for meetings between the various attendees was very valuable for promoting collaborations. A bit later start on Sunday morning would have advocates (registration was at 7:30 a.m. this year).

Some thought that discussion sessions worked better when there was a panel at the front of the room instead of simply a moderator. This should include the speakers on that topic as well as folks from industry. It was suggested that panels of workers from industry work well and are complementary to University presentations that can generally go into more detail than an industrial speaker would usually venture.

Some suggestions were made for the 15^{th} workshop. These included better food, especially some fruit in the morning. Real towns such as Breckenridge or Beaver Creek are preferred to isolated conference sites. We could pay more attention to having wireless microphones available throughout the room, and to encouraging the discipline to talk at the microphones during questions and discussion sessions.

A contingent believes that fast Internet access is a requirement for a prime meeting site.

An interesting idea was proposed that would really put the "work" back into this workshop. This was to collect questions that need answers, and break up into groups to "work" on them, before reporting results to the entire workshop. One example of the type of problem that our workshop has not been addressing is how an industrial person can maintain multiple cell testers in order to "guarantee" a minimum acceptable cell performance to the customer. Questions to work on could span from the very practical to the very fundamental.

Along the same lines, perhaps it would be useful to invite tutorial talks on topics now becoming familiar in the PV industry, such as six-sigma equipment qualifications and design of experiment (DOE) methodologies.

Perhaps we could entice manufacturers to attend the workshop by having a manufacturer's night defined in the program.

Input for the NREL University Initiative

The current set of DOE/university contracts in the silicon area is coming to a close. A new RFP is going out in the next month or so. We had an open discussion on potential topics and priorities where those remaining at this last session (about 60 of 120 that had registered) saw the greatest potential of university contributions. At the end of the discussion, votes were taken, with three votes per person in the room.

Table 1. Suggestions for potential University research contributions. Columns add to 100%. Last time, only six areas were voted on.

Last prioritization, 3 years ago (%)	**% Votes, 2004**	**Topic**
10	15	Hydrogenation, low-cost tools and improved understanding
10	14	Handling and processing thin wafers
20	13	Neutralize bad regions in wafers
10	8	Rear surface passivation
20	7	New emitters; selective, heterojunction
	7	Other fundamentals
	6	Alternatives to sawing wafers
30	5	Improved screen printing
	5	Metrology
	5	New cell structures (such as n-based)
	4	Feedstock
	4	Materials (interconnects and contacts).
	3	Heterojunction emitters on multicrystalline wafers
	2	Techniques specific to large-area cells
	1	Inline diffusion
	1	Cassette-less processes

Interestingly, the priorities seem a bit different than the last time that we did this. In particular, improved screen-printing moved down from the top of the list into the pack, and hydrogenation moved up to the top.

Input for the DOE White Paper

Some comments on the white paper contents.

1. Don't hesitate to think big, but justify the numbers by being very specific about the potential payoff. For example, an investment of $50M would cut the time in half until solar electric reached 20% of power generation (or whatever).
2. Detail the reasons why silicon will be around for a while.
3. The white paper should address the compelling reasons for strengthening the university programs. What could be done with 2X funding, 5X funding, etc.?
4. Emphasize what is new and different in the current situation.

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13. SUPPLEMENTARY NOTES

14. ABSTRACT *(Maximum 200 Words)*
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